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CONTENTS

Editorial

Radioactive Fallout Controversy 153C

Technical Papers

N-Halogen Organic Compounds as Cathode Materials for Primary Batteries. *C. K. Morehouse and R. Glicksman* 467

The Corrosion of Single Crystals and Recrystallized Single Crystals of Iron and Steel in Citric Acid. *W. R. Buck, III, and H. Leidheiser, Jr.* 474

Kinetic Studies on Formation of Black-Oxide Coatings on Mild Steel in Alkaline Nitrite Solutions. *R. M. Hurd and N. Hackerman* 482

Annealing Anodic Ta_2O_5 Films. Changes in Dissolution Behavior and X-Ray Scattering. *D. A. Vermilyea* 485

A Study of Cathode Potentials in Aqueous Tungstate Solutions. *D. R. Markwell and M. L. Holt* 488

Investigations on the Structure of the Color Compound in Caustic. *S. Wawzonek and D. S. P. Eftax* 494

Electrolytic Reduction of Nitrobenzene to Hydrazobenzene. *K. Sugino and T. Sekine* 497

The Equilibrium between Titanium Metal, $TiCl_2$, and $TiCl_3$ in NaCl-KCl Melts. *W. C. Kreye and H. H. Kellogg* 504

Determination of the Standard Free Energy of Formation of Cuprous Sulfide at 300°C. *J. B. Wagner and C. Wagner* 509

Zinc Standard Potential in Water-Organic Mixtures. *G. Corsaro and H. L. Stephens* 512

Preparation of Pure Fused Lithium Chloride-Potassium Chloride Eutectic Solvent. *H. A. Laitinen, W. S. Ferguson, and R. A. Osteryoung* 516

Technical Note

Crystal Structures of Transition Metal Silicides. *C. H. Dauben* 521

Technical Review

Review of Articles on Luminescence for 1955-1956. *G. R. Fonda* 524

Technical Feature

Hydroelectric Power in Quebec and the Atlantic Provinces. *H. Massue* 531

Current Affairs

Complete Buffalo Meeting Program 157C
Candidates for Society Offices—1958-1959 ..... 175C

Section News 176C
Division News 177C
New Members 177C
Personals 178C
ECS Membership Statistics 178C
News Items 179C
Book Review 180C
Meetings of Other Organizations 181C
Announcements from Publishers 181C
Employment Situations 182C

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Editorial

Radioactive Fallout Controversy

FALLOUT from nuclear explosions may be divided into three types. First, the smaller bombs throw debris a few miles into the air, and most of it falls to the earth's surface within a few days. These weapons can be tested in such a way that most of the fallout occurs on uninhabited areas. Second, larger explosions throw debris higher, where it may be driven by winds until it partly encircles the earth in west-to-east bands. Third, the largest thermonuclear bombs throw debris far into the stratosphere, where some of it may be spread over the entire earth and take up to 10 years to fall to the ground.

Various protests against the testing of nuclear weapons led Atomic Energy Commissioner W. F. Libby, last spring, to reiterate that the AEC is well aware of the dangers of exposing the whole world's population to extra radiation. The Commission has collected, and is collecting, as much quantitative information as possible; has studied the problem from all angles, and has reached the conclusion that these tests involve a calculated risk, which, for the present at least, is well worth taking.

While *any* avoidable exposure to radiation is undesirable, and it is especially undesirable to raise the world radiation level above the natural "pre-atomic age" background, it is agreed that the present rate of testing atomic weapons would not, for many years, result in general exposure exceeding the upper limit suggested by the National Academy Committee. However, there is another danger: Sr-90, a 0.6 mev beta-emitter with half-life of 19.9 years, is among the fission elements. Being chemically similar to calcium, strontium is taken up by plants, especially from Ca-deficient soils. If these plants are eaten by humans, or by cows whose milk is used by humans, the radioactive Sr is deposited in bones or bony tissue along with Ca. This is a danger to the individual rather than to his offspring, since few of the rays can reach the gonads. It could be especially dangerous to small children on a milk diet.

Radium is also chemically similar to calcium, and we well remember the unfortunate New Jersey women who, around 1930, died lingering deaths after ingesting Ra-containing clock-dial paint. At about the same time, Ra-containing chocolate bars were sold in Germany, radioactive soda water in the United States.

Very little is really known at present about the effect of radiation on gene mutation in humans, or about its effect on the future race. It has been assumed that more children will be born with mental and physical handicaps, with allergies and chemical inadequacies, etc. Observation of the Nagasaki and Hiroshima survivors' children does not seem to bear this out. In the U. S. there are some five million people at or below the "high-grade moron" level. (It is estimated that controlled breeding could not entirely eliminate the low IQ strains in 2,000 years.) It is feared that radiation-induced mutations could increase the percent of mentally and physically deficient groups until they became an intolerable burden on society throughout the world.

(Continued on next page)

Editorial (continued)

Balanced against this pessimistic view is the hope that nuclear weapons and the means of using them quickly and effectively will make war unthinkable to every nation. The free countries must continue research, including tests when deemed necessary, until world-wide agreement is reached, or until the results are proved too dangerous. Protests from the governments of Japan, India, and other nations must be countered with the facts. Pleas from such eminent and respected persons as Albert Schweitzer, Linus Pauling, Adlai Stevenson, Pope Pius XII, must be directed toward enforceable international agreement, not unilateral discontinuance of nuclear tests. It must never be forgotten that the enemy leaders, in the context of our civilized world, are unscrupulous gangsters, unmitigated liars whose spoken or written word cannot be trusted; the language they understand is the power to use force.

The world has not banned automobiles, which are responsible for 40,000 deaths and many times this number of injuries each year in the United States alone. Many modern developments are dangerous, but also make the existence and well-being of large populations possible. The control of nuclear reactions will be of great service to humanity, and it is important that no group in any nation treat the accompanying threat with ignorance or contempt. To insure this, the free nations must not take second place in research.

—CVK

FUTURE MEETINGS OF
The Electrochemical Society

Buffalo, October 6, 7, 8, 9, and 10, 1957

Headquarters at the Statler Hotel

Sessions will be scheduled on
Batteries, Corrosion, Electrodeposition (symposium on "Metal Powders"),
Electrodeposition—Corrosion (Joint Symposium on
"Corrosion of Electrodeposited Metals"),
Electronics (Semiconductors),
Electro-Organics, and Electrothermics and Metallurgy

★ ★ ★

New York, April 27, 28, 29, 30, and May 1, 1958

Headquarters at the Statler Hotel

Sessions probably will be scheduled on
Electric Insulation, Electronics,
Electrothermics and Metallurgy, Industrial Electrolytics,
and Theoretical Electrochemistry

★ ★ ★

Ottawa, September 28, 29, 30, October 1, and 2, 1958

Headquarters at the Chateau Laurier

★ ★ ★

Philadelphia, Pa., May 3, 4, 5, 6, and 7, 1959

Headquarters at the Sheraton Hotel

★ ★ ★

Papers are now being solicited for the meeting to be held in New York, N. Y., April 27-May 1, 1958. Triplicate copies of each abstract (*not exceeding 75 words in length*) are due at the Secretary's Office, 1860 Broadway, New York 23, N. Y., *not later than January 2, 1958* in order to be included in the program. *Please indicate on abstract for which Division's symposium the paper is to be scheduled.* Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at 1860 Broadway, New York 23, N. Y.

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BETTER THINGS FOR BETTER LIVING
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N-Halogen Organic Compounds as Cathode Materials for Primary Batteries

C. K. Morehouse and R. Glicksman

RCA Laboratories, Radio Corporation of America, Princeton, New Jersey

ABSTRACT

The electrochemical characteristics of a number of N-halogen organic compounds were studied in various electrolytes. Many of these compounds have greater theoretical ampere-minute capacity per unit of weight than the corresponding halogens, or the inorganic cathode materials used at present in primary cells. Of the compounds studied, cyclic ureides and melamine derivatives have the most promising characteristics for use as cathode materials in primary cells. Electrodes composed of these materials operate during current flow at potentials approximating the halogen-halide couple, and give in an $AlCl_3$ electrolyte ampere-minute per gram capacities corresponding to a two-electron change per "positive" halogen in the molecule.

Experimental N, N'dichlorodimethylhydantoin-magnesium reserve-type cells have been constructed and shown to operate over a wide range of current densities at potentials above 2.0 v, giving capacities over 45 whr/lb.

The desirable electrochemical properties of a cathode material for a primary cell are: (*a*) a high, reversible electrode potential, (*b*) low polarization during current flow, and (*c*) a high ampere-minute capacity per unit of weight and volume. The reversible electrode potential can be determined by the change in free energy of the cathodic half-cell reaction, while the ampere-minute capacity is directly proportional to the number of Faradays per mole involved in the reduction, and inversely to the molecular weight of the cathode material.

In addition, certain physical and chemical properties of a cathode material such as solubility, stability, and physical form are important in determining its use in a particular type of primary cell. For example, materials which have a high solubility, or low stability in the electrolyte, would be unsuitable for use in dry cells, but might find application in reserve cells of the type which are stored dry and activated just prior to use by adding the electrolyte or water.

The halogens are attractive materials for use as cathodes in batteries, because of their high electrode potential during current flow, and high ampere-hour capacity per unit of weight and volume. The disadvantages to the use of these materials are obvious. Fluorine and chlorine are highly toxic and corrosive gases, bromine a volatile liquid, and iodine a solid with a high vapor pressure. Many attempts (1-9) have been made to utilize these materials in electrochemical batteries, but to date the difficulties associated with their handling have not been overcome to enable the design of a practical battery.

The hypohalous acids and their salts have higher reversible electrode potentials and ampere-minute capacities per unit of weight than their corresponding halogens. However, because of their low stability, or high solubility, they are unsuitable for primary cells.

The N-halogen organic compounds have been found to have similar electrochemical properties to those of the hypohalous acids and their salts. These organic compounds can be considered as substituted ammonia analogues of hypohalous acid. Many of them are considerably more stable than their corresponding inorganic hypohalites and, therefore, are more attractive for use as cathode materials in primary cells.

Arsem (10) described dry cells containing a few N-halogen organic compounds as cathodes coupled with a Zn anode. No other reference has been found in the literature referring to the application of these compounds to electrochemical power supplies.

In this paper a survey of the electrochemical properties of various types of N-halogen organic compounds is presented, along with data obtained on experimental reserve cells containing one of the more promising materials as a cathode coupled with a Mg anode.

Electrochemical Characteristics

A typical example of a N-halogen organic compound and the manner in which the halogen is held in the molecule is shown by the equation:

$$R{:}\dot{\underset{\cdot\cdot}{N}}{:}H + Cl^+Cl^- \rightarrow R{:}\dot{\underset{\cdot\cdot}{N}}{:}H + H^+ + Cl^- \qquad (I)$$

The chlorine atom attached to the N is described as a "positive" halogen and resembles that attached to oxygen as in hypochlorous acid, since on hydrolysis it combines with the negative hydroxide ion to form hypochlorous acid.[1] It is reasoned that reactions taking place at an electrode containing a N-halogen organic compound could proceed through the hydrolysis stage, followed by subsequent re-

[1] A test for a "positive" halogen organic compound is to dissolve the compound in an aqueous solution of acetic acid and an iodide and titrate the iodine liberated. Two iodine atoms are liberated for every "positive" halogen.

duction of the hypohalite ion. There is also some experimental evidence which indicates that the electrode mechanism might be through the direct reduction of the N-halogen compound. Equations and reversible electrode potentials given by Latimer (11) for possible reactions of a N-halogen organic electrode in halide electrolytes are given below, using two mechanisms.

Hydrolysis:

$$RNHX + HOH = RNH_2 + HOX \qquad (II)$$

Basic solutions:

$$ClO^- + H_2O + 2e^- = 2OH^- + Cl^- \quad E^\circ_R = 0.89 \qquad (III)$$

$$BrO^- + H_2O + 2e^- = 2OH^- + Br^- \quad E^\circ_R = 0.76 \qquad (IV)$$

Acidic solutions:

$$HClO + Cl^- + H^+ = Cl_2 + H_2O \qquad (V)$$

$$Cl_2 + 2e^- = 2Cl^- \qquad E^\circ = 1.36 \qquad (VI)$$

$$HClO + 2Br^- + H^+ = Br_2 + H_2O + Cl^-$$
$$HBrO + Br^- + H^+ = Br_2 + H_2O$$
$$Br_2 + 2e^- = 2Br^- \qquad E^\circ = 1.09 \qquad (VII)$$

Direct Reduction:

$$RNHX + H_2O + 2e^- = OH^- + X^- + RNH_2 \qquad (VIII)$$

$$RNHX + H^+ + 2e^- = RNH_2 + X^- \qquad (IX)$$

$$RNHX + X^- + H^+ = RNH_2 + X_2$$
$$X_2 + 2e^- = 2X^- \qquad (XI)$$

Experimental Results

Most electrode reactions do not function at their reversible electrode potentials because of the irreversible nature of the reaction and polarization effects encountered when operating an electrode at a relatively high current density. Since many inorganic and organic reactions are known to be irreversible and their electrode potentials during cur-

Table I. Capacity data for various N-halogen organic cathode materials

Cathode material	Source (see foot notes)	% "Active" halogen Actual	% "Active" halogen Theoretical	Amp-min/g capacity Theoretical*	Amp-min/g capacity Obtained†	Efficiency‡ %
Chlorine	—	50	50	45.4	—	
Bromine	—	50	50	20.1	—	
	N-halogen organic compounds					
Amides						
(a) *Carboxylic acid*						
N-bromoacetamide	1	57	57	23.3	3.0	12.9
N-bromobenzamide	1	39.3	39.9	13.6	6.3	47.0
N, N'dibromoterephthalamide	1	43.7	49.7	19.8	6.6	38.0
N, N'dibromooxamide	1	60.5	65.2	26.1	0.6	2.5
N, N'dibromosuccinamide	1	57.5	58.3	23.5	2.4	10.3
N, N'dibromoadipamide	1	51.3	53.1	21.3	7.3	35.7
(b) *Sulfonic acid*						
N-chloro-p-toluenesulfonamide, sodium salt	2	—	12.8	11.4	0.2	1.7
N, N dichloro-p-toluenesulfonamide	2	—	29.6	26.8	14.1	52.6
N, N dibromo-p-toluenesulfonamide	1	46.1	48.5	19.7	6.0	31.9
N, N dichloro-p-benzenesulfonamide	1	31.5	31.3	28.3	11.7	40.9
N, N dichloro-p-carboxylic acid benzenesulfonamide	3	—	26.3	23.8	5.7	23.9
Imides derived from dibasic acids						
N-chlorosuccinimide	2	—	26.6	24.1	11.7	48.5
N-bromosuccinimide	4	—	45.9	23.3	9.0	38.6
N-bromophthalimide	1	33.2	35.3	14.2	4.7	35.1
Amides of carbonic acid (urea)						
(a) *Straight chain*						
N, N'dichlorobiuret	1	—	41.3	37.4	~15.0	~40.1
(b) *Cyclic*						
Trichloroisocyanuric acid	5	44.7	45.8	41.5	10.2	25.3
3 Bromo,5,5 dimethylhydantoin	1	38.5	38.6	15.5	7.5	48.4
N, N'dibromodimethylhydantoin	1	55.	55.9	22.3	10.9	49.9
N, N'dichlorodimethylhydantoin	6	33.	33.	32.6	15.0	46.0
N, N'dichlorodiphenylhydantoin	6	16.	22.1	20.1	6.3	43.1
N, N'dibromodiphenylhydantoin	1	38.	39.0	15.6	7.5	49.5
N, N'dibromobarbituric acid	1	—	55.9	22.5	3.6	16.0
Amidines of carbonic acid (guanidine)						
N-chlorodicyandiamide	5	15.	30.3	27.1	~0.1	0.8
Trichloromelamine	7	44.5	46.4	42.2	~18	43.9
Tribromomelamine	7	65.3	66.7	26.6	10.9	41.8
Hexachloromelamine	7	—	64.0	58.0	~19.5	33.6

† Computed from half-cell data in Fig. 1-6 incl. using 0.20 v as an arbitrary end point.
* Theoretical capacity computed from theoretical "active" halogen content.
‡ Efficiency computed on basis of actual "active" halogen content of compound.
[1] Arapahoe Chemicals, Inc.
[2] Matheson, Coleman & Bell.
[3] Abbott Laboratories.
[4] Fisher Scientific Co.
[5] American Cyanamid Co.
[6] Wyandotte Chemicals Corp.
[7] Wallace & Tiernan, Inc.

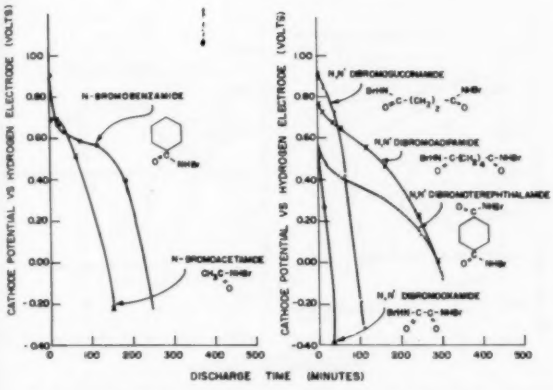

Fig. 1. Cathode potential-time relationship of various mono and dibasic carboxylic acid amide N-bromo derivatives discharged in 250 g/l $MgBr_2 \cdot 6H_2O$ electrolyte at a rate of 0.030 amp/g.

rent flow cannot be predicted by thermodynamic calculations, other methods have to be used to evaluate new materials. A technique, previously described (12), was used to study the electrochemical properties of a number of N-halogen organic compounds. This consists in discharging at a constant current drain, in a large volume of electrolyte, a 0.5-g sample of the cathode material mixed with carbon. The potential of the cathode was measured against a saturated calomel reference electrode with a L&N Type K potentiometer.

Half-Cell Discharge Data for Various N-Halogen Organic Compounds in a $MgBr_2$ Electrolyte

Half-cell data obtained on various N-halogen organic compounds discharged continuously at a 0.030 amp/g rate[2] in a $MgBr_2 \cdot 6H_2O$(250 g/l) electrolyte are shown in Fig. 1-6 inclusive. The data given include an *IR* drop amounting to 0.08 v due to the resistance of electrolyte and apparatus. No correction was made for temperature variation of the saturated calomel electrode which would amount to no more than ±0.01 v.

The capacity obtained to an arbitrary 0.20 v cut off potential (vs. S.H.E.) under current drain along with their electrode efficiencies is presented in Table I together with the theoretical capacities of these materials expressed in ampere-minutes per gram.

[2] The current flow was expressed in this manner because of the difficulty associated with determining the true surface area taking part in the electrochemical reaction, which value is necessary in order to express the current density in amperes per unit area.

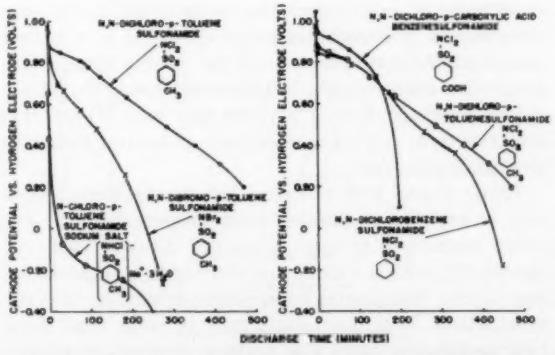

Fig. 2. Cathode potential-time relationship of various N-halogen derivatives of sulfonic acid amides discharged in 250 g/l $MgBr_2 \cdot 6H_2O$ electrolyte at a rate of 0.030 amp/g.

Acid amides of the type RCOHNX.—Table I shows that four of the six listed N-bromo carboxylic acid amides have theoretical capacities greater than that of elemental bromine. However, the actual capacities obtained from these compounds are considerably lower than theoretical, ranging from 0.6-7.3 amp-min/g, with efficiencies ranging from 2.5 to 47%. Also, the efficiencies of the N-bromo aromatic carboxylic acid compounds are greater than those of the alkyl carboxylic acid compounds. This is probably due to the greater stability and lower solubility of the aromatic compounds in the electrolyte. This relationship is even more evident when one considers the capacities and efficiencies of the homologous series of alkyl N, N′ dibromo dibasic acids. Under conditions of discharge, the cathode efficiency of these compounds increases as the chain length of the dibasic acid increases, while there is a corresponding decrease in solubility as one goes from N, N′ dibromooxamide to N, N′ dibromoadipamide.

The half-cell discharge curves in Fig. 1 show that the potentials of these electrodes range from 0.60-0.90 v initially, but decrease rapidly under current drain.

Sulfonic acid amides of the type RSO_2NHX.—Discounting the data for the soluble sodium salt of N-chloro-p-toluenesulfonamide (Chloramine T), it is seen in Table I that capacities ranging for 5.7 to 14.1 amp-min/g were obtained from compounds of this class, with corresponding efficiencies of 23.9-52.6%, respectively. Because of their higher capacities and efficiencies, this class of N-halogen compounds has greater promise as cathode materials for primary cells than the previously discussed carboxylic acid amides, the best of these materials being N, N dichloro-p-toluenesulfonamide (Dichloramine T).

Half-cell data obtained on various N-halogen derivatives of sulfonic acid amides are presented in Fig. 2. As expected, the N-chloro derivatives operate at a higher potential and give a greater ampere-minute per gram capacity than the corresponding N-bromo compounds, as evidenced by the half-cell discharge data obtained on N, N dichloro-p-toluenesulfonamide and N, N dibromo-p-toluenesulfonamide. The poor performance of the sodium salt of N-chloro-p-toluenesulfonamide as a cathode material is probably due to the high solubility of this compound in the $MgBr_2$-H_2O electrolyte.

Also shown are half-cell data obtained on N, N dichlorobenzenesulfonamide, N, N dichloro-p-carboxylic acid benzenesulfonamide, and N, N dichloro-p-toluenesulfonamide, these compounds differing from one another only in the type of para substituted group. It is seen that the carboxylic acid compound has a higher potential initially, probably as a result of the effect of the acidic group on its potential.

Imides of the type $(RCO)_2NHX$.—Diacyl derivatives of ammonia, $(RCO)_2NH$, known as imides, also have a hydrogen attached to the nitrogen atom,

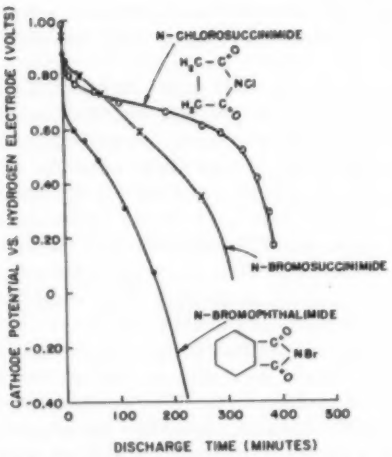

Fig. 3. Cathode potential-time relationship of various N-halogen imide derivatives discharged in 250 g/l $MgBr_2 \cdot 6H_2O$ electrolyte at a rate of 0.030 amp/g.

which is replaceable by a halogen atom to form the N-halogen derivative. Typical examples of this class are the N-chloro-, and N-bromosuccinimide, and phthalimide compounds. Capacity data for these materials are tabulated in Table I and half-cell discharge data shown in Fig. 3. These compounds had discharge characteristics similar to the previously discussed N-halogen acid amides. Of the three imides tested, N-chlorosuccinimide had the most favorable discharge characteristics.

Amides of carbonic acid (urea derivatives).—There are many urea derivatives which also have a replaceable hydrogen attached to the nitrogen atom, and thus are capable of forming N-halogen compounds. N, N′ dichlorobiuret is an example of a straight chain compound of this class, whereas trichloroisocyanuric acid, N, N′ dichlorodimethylhydantoin, and N, N′ dibromobarbituric acid are examples of cylic derivatives. All of these compounds have the characteristic property of the other N-halogen compounds cited, in that they are strong oxidizing agents.

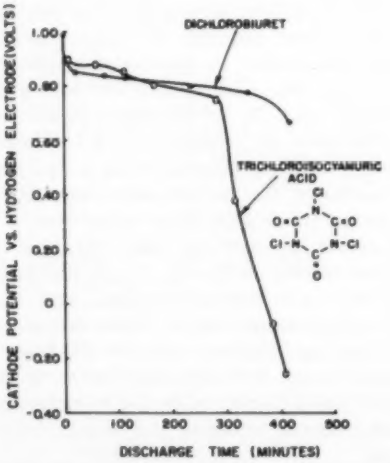

Fig. 4. Cathode potential-time relationship of various N-halogen urea derivatives discharged in 250 g/l $MgBr_2 \cdot 6H_2O$ electrolyte at a rate of 0.030 amp/g.

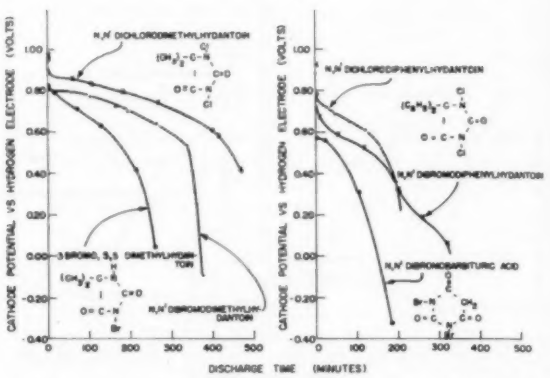

Fig. 5. Cathode potential-time relationship of various N-halogen cyclic urea derivatives discharged in 250 g/l $MgBr_2 \cdot 6H_2O$ electrolyte at a rate of 0.030 amp/g.

Among the cyclic urea derivatives tested, the hydantoin compounds are of particular interest because of their relatively high electrode efficiencies in the $MgBr_2$-H_2O electrolyte as shown in Table I. These compounds, measured at the 0.030 amp/g rate, had efficiencies ranging from 43-50%, which values are greater than those obtained for the other two cyclic urea derivatives tested. An efficiency of 40% was also obtained from the straight chain dichlorobiuret compound, which along with N, N′ dichlorodimethylhydantoin are the most promising compounds of this group because of their high flat voltage vs. time discharge curves (Fig. 4 and 5) and high theoretical and experimentally obtained ampere-minute per gram capacities.

Discharge curves for the various N-halogen hydantoin derivatives are shown in Fig. 5, and as expected the chloro compounds operate at higher potentials during current flow than the corresponding bromo compounds, while the monobromo compound has a potential lower than its corresponding dibromo compound.

Amidines of carbonic acid (guanidine derivatives).—Four compounds of this class, trichloro- and tribromomelamine, hexachloromelamine, and N-chlorodicyandiamide, all of which are solids at ordinary temperatures, have been evaluated, data being presented in Fig. 6 and Table I. N-chlorodicyandiamide performed poorly as a cathode material, probably because of low stability under the conditions of evaluation. As with other N-halogen compounds, trichloromelamine operated at a higher potential than its corresponding bromo compound, while the more highly halogenated hexachloromelamine operated during current flow in a $MgBr_2$-H_2O electrolyte at a higher electrode potential than the trichloromelamine.

From Table I it is seen that trichloromelamine and hexachloromelamine gave ampere-minute per gram capacities of approximately 18 and 19.5, respectively, which values are the highest obtained on any of the N-halogen compounds tested in this investigation. It is also significant to note that these two melamines have the highest theoretical capacity of all the N-halogen compounds considered, the capacity of hexachloromelamine being 28% greater

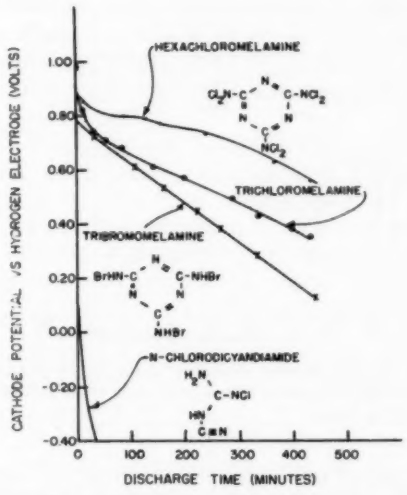

Fig. 6. Cathode potential-time relationship of various N-halogen guanidine derivatives discharged in 250 g/l $MgBr_2 \cdot 6H_2O$ electrolyte at a rate of 0.030 amp/g.

than the theoretical ampere-minute per gram capacity of chlorine.

Half-Cell Discharge Data of Three N-Halogen Organic Compounds in Various Electrolytes

It is seen from the data in Table I that in a 250 g/l $MgBr_2 \cdot 6H_2O$ electrolyte, and at a 0.030 amp/g rate of discharge, the cathode efficiency of all the organic N-halogen compounds, except N, N dichloro-p-toluenesulfonamide, was less than 50%, indicating that not all the chlorine atoms are taking part in the electrode reaction.

Analytical data obtained by dissolving weighed samples of trichloromelamine in glacial acetic acid and in water, adding an excess of potassium iodide and titrating the iodine liberated in each solution showed that in the glacial acetic acid solution the "active" halogen content in the molecule was 44.5%, which corresponded to a two electron change per chlorine atom, whereas in a water solution the liberated iodine corresponded to only 24.3% of the "active" chlorine. In neutral or water solution a fading end point was observed in the titration of the iodine, indicating that the slow hydrolysis of trichloromelamine was the cause of the low value for the "active" chlorine content in the molecule.

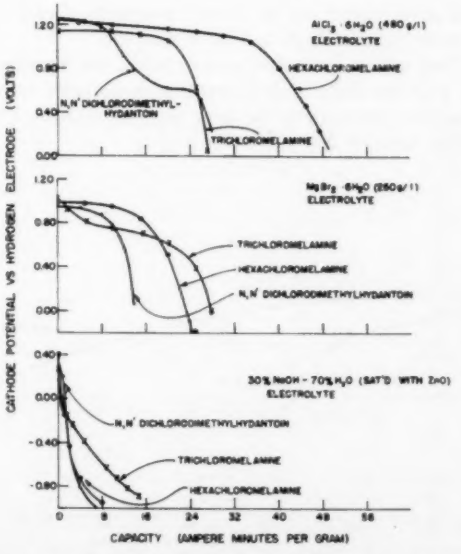

Fig. 7. Cathode potential-capacity relationship of three N-halogen organic compounds discharged in various electrolytes at a rate of 0.005 amp/g.

Since the electrode efficiencies of most cathodes depend on the current density and electrolyte composition, half-cell data were obtained on N, N'dichlorodimethylhydantoin, trichloromelamine, and hexachloromelamine when discharged at 0.005 amp/g rate in various electrolytes. The half-cell discharge curves are presented in Fig. 7.

Data in Fig. 7 show that the potentials during current flow of all three cathode materials increase as the acidity of the electrolyte is increased, as might be expected from an examination of the electrode reactions previously cited. In addition, the ampere-minute per gram capacities of the three cathode materials increase with increasing electrolyte acidity which is in accord with the analytical data previously discussed. In a NaOH electrolyte, the three N-halogen electrodes polarized rapidly, and operated at low electrode efficiencies. This low efficiency is believed due to the poor stability of these compounds in a strongly alkaline solution.

The coulombic capacities obtained from the discharge data in a $MgBr_2$ electrolyte (allowing an 0.8 v drop in potential from initial) correspond approximately to the reduction of one halogen in the N, N'dichlorodimethylhydantoin, and two in trichloromelamine and hexachloromelamine, assuming a two electron change per halogen atom in the molecule. Discharging the N, N'dichlorodimethylhydantoin and hexachloromelamine in the more acidic (480 g/l $AlCl_3 \cdot 6H_2O$) electrolyte resulted in a 40% increase in electrode efficiency. On the other hand, no increase in electrode efficiency was obtained from the trichloromelamine electrode, although a more favorable type of discharge curve was obtained in the $AlCl_3$ electrolyte.

The two step discharge curve of the N, N'dichlorodimethylhydantoin accounts for its large increase in efficiency in the $AlCl_3$ electrolyte, since both active halogen atoms are now being utilized, whereas in the $MgBr_2$ electrolyte apparently only one halogen atom took part in the reduction. From the chemical structure of this compound, one would expect the chlorine on the nitrogen atom adjacent to the two carbonyl groups to be more easily reduced than the other "active" halogen in the molecule, thereby accounting for the two step reduction.

Cathode efficiencies computed for the discharge of trichloromelamine and hexachloromelamine in the $AlCl_3$ electrolyte indicate a reduction of 2 and 5 halogen atoms, respectively; apparently the last halogen on the melamine molecule is extremely difficult to reduce.

Comparison with Conventional Cathode Materials

Half-cell discharge data obtained at a 0.005 amp/g rate for two of the more promising N-halo-

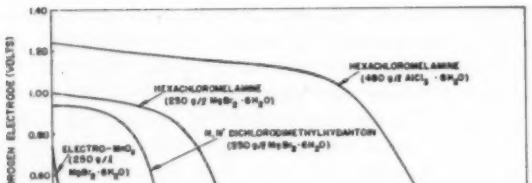

Fig. 8. Comparison of cathode potential-capacity relationship of various N-halogen organic and conventional inorganic cathode materials discharged at a rate of 0.005 amp/g in compatible electrolytes.

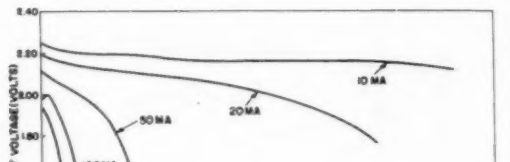

Fig. 9. Constant current discharge curves for N, N'dichlorodimethylhydantoin-magnesium reserve cells (cast type). [Approx. vol. 4 cm³, wt 5.0 g (wet).]

gen compounds compared with three cathode materials now used in commercial primary cells are shown in Fig. 8. These data show that the hexachloromelamine and N, N'dichlorodimethylhydantoin in both a $MgBr_2$ and an $AlCl_3$ electrolyte operate at considerably higher potentials than electrolytic manganese dioxide, cuprous chloride, or silver (II) oxide cathodes when tested in their compatible electrolytes under comparable conditions of discharge. Calculations, based on a 0.2 v drop in half-cell discharge potential show that hexachloromelamine, which theoretically has 123% and 258% greater ampere-minute per gram capacity than silver (II) oxide and cuprous chloride, respectively, gave in an $AlCl_3$ electrolyte 74% and 226% greater ampere-minute capacity per unit of weight than these cathodes discharged in their compatible electrolytes. Further improvement in the performance of the hexachloromelamine cathode should be possible as it operated under these conditions of discharge at only 58.6% efficiency.

It would be expected, from the half-cell discharge data in Fig. 8, that coupling N-halogen organic cathodes with magnesium or aluminum anodes would result in primary cells with operating potentials of 2.2 and 1.8 v, respectively.

Primary Cell Data

While it has been shown that many of the N-halogen organic compounds have attractive electrochemical characteristics, they do hydrolyze in aqueous solutions forming the soluble hypohalite. The latter property limits their use as cathodes in primary batteries assembled with an aqueous electrolyte, since the shelf life of the battery would be limited. The problem of hydrolysis during storage is not encountered in reserve cells of the type which are stored dry or in an inactive condition and activated prior to use by adding the electrolyte.

N, N' dichlorodimethylhydantoin, a stable solid which can be sublimed at 130°C without decomposition, and has a low solubility in aqueous solutions (0.21 g/100 g H_2O at 25°C) was selected for trial in reserve batteries. Cathodes were constructed by taking an intimate mixture of 2 parts by weight of the material and 1 part by weight of graphite and heating to the melting point of the N, N'dichlorodimethylhydantoin. The resulting viscous mixture was poured into a paper-lined can (I. D. 0.395 in., height 1.824 in.), a carbon rod (O. D. 0.100 in., height 1.824 in.) inserted, and the mass allowed to solidify. The formed electrode was removed from the can, wrapped first with a piece of absorbent nonwoven fabric (Kendall-Mills) material, then with 0.010 in. thick magnesium sheet. The cell was held together by binding with wire. The approximate dimensions of the completed cell were: height, 1¼ in.; diameter, ½ in.; volume, 4 cm³ (0.25 in.³); weight of cathode, graphite, and carbon rod, 2.0 g; weight of cathode material, 0.7 g; weight of cell (dry), 4.0 g; weight of cell (wet), 5.0 g.

The above cells were activated by immersing them in an aqueous solution of $MgBr_2 \cdot 6H_2O$ (250 g/l) and $Na_2Cr_2O_7$ (1.0 g/l). The discharge data obtained on cells of this construction are shown in Fig. 9. The data show that these N, N'dichlorodimethylhydantoin-magnesium reserve cells operate above 2.0 v over a wide range of current drains, and give capacities of 1.1-3.2 w-min/cm³ and 0.9-2.6 w-min/g, based on a 1.80 v cut off.

Flat cells were also constructed by pasting 3.8-4.5 g of the following cathode mix on both sides of a graphite plate (1¼ in. long x 1 in. wide x 1/16 in. thick, weight 2.0 g).

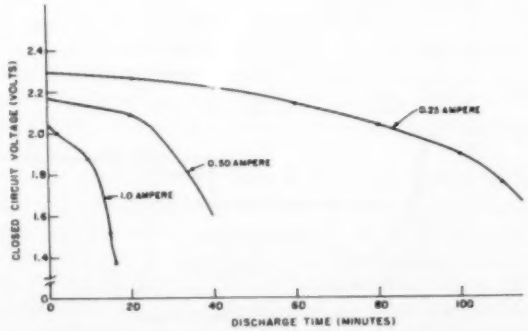

Fig. 10. Constant current discharge curves for N, N'dichlorodimethylhydantoin-magnesium reserve cells (flat type). [Approx. vol. 5 cm³, wt 10 g (wet).]

N, N'Dichlorodimethylhydantoin,	0.96-1.13 g
Shawinigan acetylene black,	0.56-0.48 g
$MgBr_2 \cdot 6H_2O$ (500 g/l) + $Li_2CrO_4 \cdot 2H_2O$ (1.0 g/l) electrolyte,	2.4 -2.8 g

The above cathode was wrapped with a piece of absorbent Kraft paper and then with magnesium sheet (3 in. long x 1 in. wide x 0.010 in. thick, weight 1.0 g). The approximate weight of the cell after activating with magnesium bromide electrolyte was 10 g and occupied a volume of approximately 5.1 cm^3(0.311 $in.^3$). Discharge characteristics of cells of this design are shown in Fig. 10. Capacities of 5.3-12.1 w-min/cm^3 and 2.7-6.2 w-min/g were obtained from these cells at current drains ranging from 1.0-0.250 amp.

Cells made by the two constructions described above represent laboratory samples and performance characteristics which can be expected from reserve cells using N-halogen organic compounds as cathode materials. These data, while not representing a completed development, point to the possibility of developing batteries utilizing relatively inexpensive materials which will give performance characteristics superior to existing reserve-type batteries.

Acknowledgment

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1958 JOURNAL.

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The Corrosion of Single Crystals and Recrystallized Single Crystals of Iron and Steel in Citric Acid[1]

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ABSTRACT

Corrosion studies, largely in 0.2M citric acid at 20°C and the boiling point, were made on polycrystalline disks and monocrystalline spheres and disks of Armco iron and type L steel. Preliminary experiments indicated that the (100) face corroded at the slowest rate and the minor faces, of which the (321) is an example, corroded at the most rapid rate. Quantitative measurements were confined to these two crystal faces. The (100) face was cathodic to the (321) face as shown by potential measurements in 0.2M citric acid in the presence and absence of air. The rate of corrosion of the (321) face was approximately twice that of the (100) face on specimens which were chemically polished, electrolytically polished, machined with a sharp lathe tool, or polished with emery paper. The rates of corrosion of the polycrystalline starting material from which the single crystals were prepared were several times greater than those of the single crystals. Conversion of the single crystals to polycrystalline material by heating through the transformation temperature resulted in a considerably increased corrosion rate. In the presence of 40-45 ppm of Sn(II) the rates of corrosion of the single crystals in 0.2M citric acid at the boiling point were reduced greatly and no significant difference between the (100) and (321) faces was observed.

It is generally recognized by metallurgists that different crystal faces of a metal corrode at different rates. The differentiation of grains by etching, the varying interference colors formed on the grains of polycrystalline metals during the heating in air, and the different optical properties of the oxide film formed on the various grains of polycrystalline aluminum are but three examples from this general fund of knowledge. The importance of crystal face in controlling rates of chemical reactions has been demonstrated in a large number of recent investigations using spherical and flat single crystals (2-6); only a few of those with which the authors are more intimately concerned are mentioned here. The majority of such investigations have been qualitative in nature and only very limited quantitative information is available on the relative rates of corrosion of different crystal faces in liquid corrosion media. The only paper which is directly related to the present work and which gives quantitative information on the rates of solution of different crystal faces of iron is that of Engell (7). He studied the current-voltage curves during anodic dissolution in acid and found that ". . . the rate of corrosion, as shown by the current density-voltage curve during dissolution of iron, in all cases investigated is independent of the orientation of the crystal surfaces at low current densities. At higher densities, on the other hand, the (111) and (110) surfaces are more greatly attacked than the cube faces by a factor of 2. The other orientations lie in their properties between these extremes."

The purposes of the present investigation were (*a*) to determine the order of magnitude of the differences between the rates of corrosion of the crystal faces of iron in a fruit acid, (*b*) to determine the factors which control the rate of corrosion, and (*c*) to compare the rates of corrosion of single crystal with polycrystalline material of the same composition.

Experimental

Single crystals of Armco iron, ⅜ in. in diameter and up to 3½ in. in length, were prepared by the anneal-strain-anneal method. Rods, ⅜ in. in diameter and 4 in. long, were etched in aqua regia and were annealed at a pressure of 30-100 μ of air for 24 hr at 850°C. After cooling, the rods were reduced 3.25% in length by compression, which was carried out in a hardened-steel cylinder to prevent bending. The rods were then heated at 890°-900°C at a pressure of 30-100 μ of air for 5-10 days. Certain mill runs had a high tendency to form crystals that covered the entire cross section; the largest crystals were obtained from these rods. The Armco crystals were prepared from stock which had a ladle analysis of: C 0.02%, Mn 0.03%, P 0.009%, and S 0.016%.

Type L[2] single crystals were grown in the rim section of cross-sectional pieces, 2½ in. x 1¼ in. x ½ in. to ¾ in. thick, of a rimmed steel having a composition within the range of specifications of L

[1] The results of a few of the experiments reported herein have been described previously (1). Because of the brevity of that communication and for the sake of completeness, those results are also included in this report.

[2] Type L steel is that specified by manufacturers for containers with the maximum corrosion resistance.

steel. The mill ladle analysis of this material was C 0.08%, Cu 0.02%, Mn 0.30%, Ni 0.01%, P 0.012%, Cr 0.01%, S 0.05%, Mo 0.00%, and Si 0.008%. A wet analysis[3] of the rim area in which the crystals grew yielded: C 0.038%, P 0.011%, Mn 0.25%, and S 0.024%. Large crystals were formed in cross-sectional pieces cut from the billet by heating them at a pressure of 30-100 μ and 850°C for 5-14 days. A photograph of a typical growth experiment is given in Fig. 1.

Corrosion measurements made at 20°C were carried out in 20 ml of acid deaerated by the freeze-thaw method of Pryor and Cohen (8). The acid solution was frozen and the system was pumped down to a low pressure with a Hg diffusion pump and thawed five times. The Fe sample was inserted into the system after the fifth freeze. Pressure measurements were made with a McLeod gauge which was separated by a stop cock and dry ice trap from the acid solution. Measurements at the boiling point were made in an assembly consisting of a 250 ml Erlenmeyer flask and a reflux condenser. After the solution (100 ml) had been boiling for several hours, the cylindrical Fe single crystal, held in a short length of Tygon tubing in order to protect the sides and edges from the action of the acid, was inserted in the Erlenmeyer flask. The crystal was held by means of a permanent magnet so that the flat surfaces were perpendicular to the bottom of the flask. This precaution was necessary in order to keep the ends of the disk freely exposed to the solution. The rate of corrosion as a function of time was determined by withdrawing small samples at intervals and making colorimetric determinations using thioglycollic acid. Weight losses at the end of the experiment served as a check on the colorimetric determinations.

Single crystal spheres, 0.9 cm in diameter, with a small shaft were machined from both the Armco rods and the L-steel slabs. Disks, 0.8 cm in diameter and 0.4-0.5 cm in thickness, whose surfaces were parallel to the (100) or (321) planes were cut from the long single-crystal rod of Armco Fe. Disks parallel to (100) and (321) planes were cut from a single grain of L-steel. Other disks parallel to the (100) and (321) planes were cut from neighboring crystals in the same piece of steel. The accuracy of the cuts was determined by back reflection x-ray analysis immediately after machining and near the conclusion of the experiments. The orientation of the flat faces was within 2° of that desired in both cases. After machining, the crystals were deeply etched and were then heated for 6-16 hr at 475°-500°C in He or in a vacuum, in order to release residual strains from the machining operation. The crystals were polished with metallographic emery paper followed by chemical polishing in Mirro-Fe[4] or in the early experiments, electrolytic polishing in the perchloric acid-acetic anhydride bath of Jacquet and Rocquet (9).

[3] The authors are indebted to the American Can Company for carrying out these analyses.

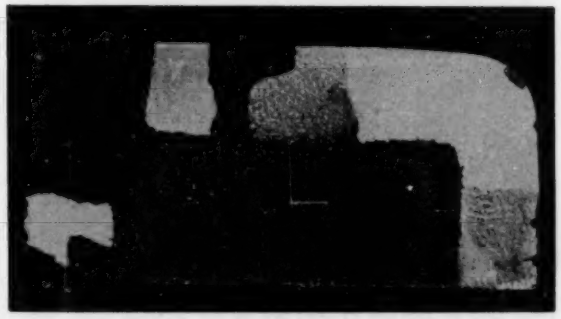

Fig. 1. Typical large grains formed in the rim area of half of a cross-sectional piece cut from a billet of L-steel.

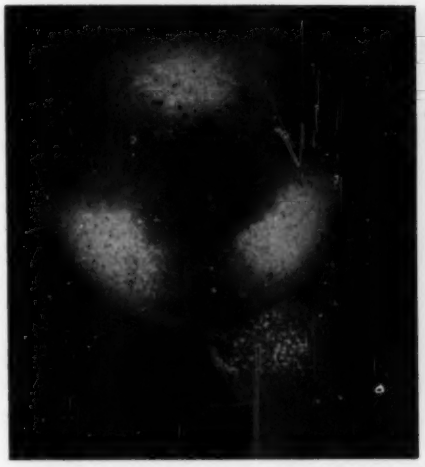

Fig. 2. Typical etch pattern on an Fe single-crystal sphere immersed in citric acid.

Preliminary Experimental Results

Results with spheres.—In order to choose experimental conditions and crystal faces for the quantitative study, single-crystal spheres were immersed for observation in citric acid solutions ranging from 0.002M to saturation, at temperatures from 25° to 85°C, and with and without stirring. The relative behavior of the different faces was the same under all conditions. The general behavior in 0.2M citric acid at room temperature was as follows: Soon after immersion of the sphere, hydrogen bubbles began to form. After 15-30 min, an etch pattern could be seen, which increased in contrast for 12-24 hr and eventually became obscured by general corrosion. First, the large areas surrounding the (111) faces lost their original high luster. The (100) faces and a small square-shaped area around them retained the high luster for as long as 70 hr. Facets developed parallel to (100) planes only. A typical etch pattern is shown in Fig. 2. Microscopic views of the (100) face and of the area adjacent to the (111) face are shown in Fig. 3 and 4.

Spherical crystals exposed to 3M acetic acid, 3M hydrochloric acid, 1M sulfuric acid, 5% nitric acid in alcohol (nital), 3M phosphoric acid, 0.2M tartaric acid, and 0.2M oxalic acid yielded results essentially the same as those obtained in citric acid. Areas surrounding the (111) faces were the first to etch and become roughened and the (100) faces showed the slowest rate of etching. There were

[4] Obtained from MacDermid, Inc., Waterbury, Conn.

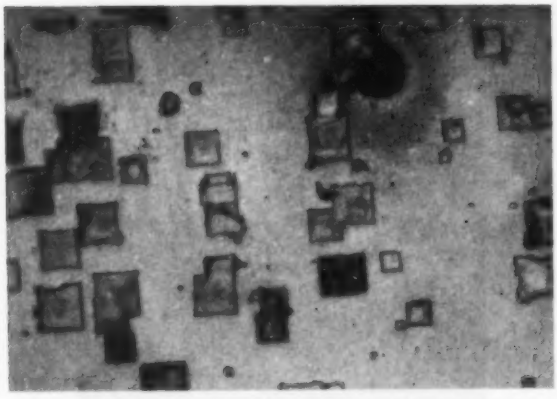

Fig. 3. Typical surface formed on (100) face of Fe when corroded in 0.2M citric acid. Magnification, 1000X.

minor differences in the details of the etch patterns with the various acids, but the great difference between the (111) and (100) areas was noted in all cases.

Previous experiments in this laboratory and at the University of Virginia offered direct proof that the rate of roughening of an electrolytically polished surface was a measure of the rate of etching. However, it was of interest to check again this conclusion. Two types of experiments bear on this problem. First, the results described in a following section on the potential measurements confirm conclusions drawn from the experiments with the spheres. Second, an experiment carried out in nital offered convincing evidence that the (100) face which roughened at the slowest rate also etched at the slowest rate. An electrolytically polished crystal sphere was immersed in nital for a total of 16 hr at room temperature. The crystal was transferred frequently to fresh solutions of nital in order to increase the rate of the reaction. At the end of the experiment the six (100) faces were raised appreciably above the surface. This result could only have been obtained if the (100) faces corroded at a slower rate than any other face.

Results observed on the various faces of the sphere were also observed on polycrystalline samples of L-steel. Grains which remained smooth during corrosion also etched at the slowest rate as shown by the fact that neighboring rough grains were at a lower level. These smooth and slow-corroding grains were identified as (100) faces from the fact that minute square pits were developed on their surfaces.

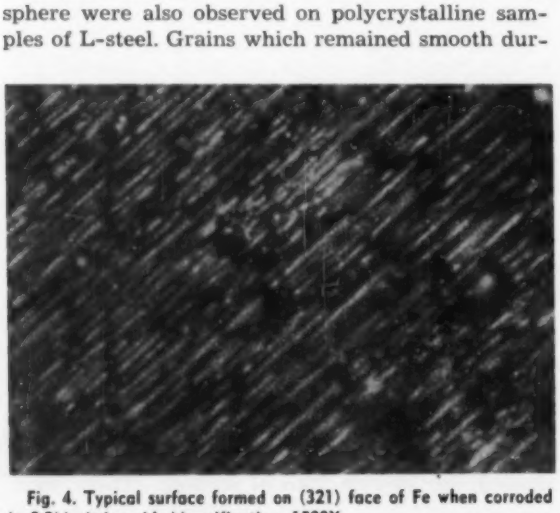

Fig. 4. Typical surface formed on (321) face of Fe when corroded in 0.2M citric acid. Magnification, 1500X.

Confirmation of the general conclusion that the rate of corrosion of the minor faces making small angles with the (111) plane was greater than the (100) face was obtained in the following experiment. A flat face parallel to a (100) plane was cut on a sphere of Armco Fe and a flat face parallel to a (321) plane was cut on a second sphere. After electrolytic polishing, the spheres were wound with Sn wire and both were connected to a Sn bar. All of the surfaces except the (100) and (321) faces of Fe and a small section of the Sn bar were coated with a waterproof lacquer. The assembly was then inserted in a gel containing 7 g commercial gelatin in 300 ml of 0.02M citric acid containing just sufficient potassium ferricyanide to give a slight color. As the Fe corroded, the products diffused through the gel and formed a blue color due to ferrous ferricyanide as shown in the photograph in Fig. 5. It will be noted in the figure that the diffusion zone around the (321) face on the right is much thicker than the diffusion zone around the (100) face on the left.

Potential Measurements

Four different types of potential measurements were made at room temperature in 0.2M citric acid. The results may be summarized in the following statements:

1. The potential difference between (100) and (321) faces of Armco Fe in solutions exposed to air ranged from 7 to 17 mv after immersion for 7-72 hr, the (100) face always being cathodic.

2. The potential difference between the (100) and (321) faces of Armco Fe in solutions deaerated by freeze-thaw cycling ranged from 3 to 8 mv after immersion for 23-92 hr, the (100) face always being cathodic.

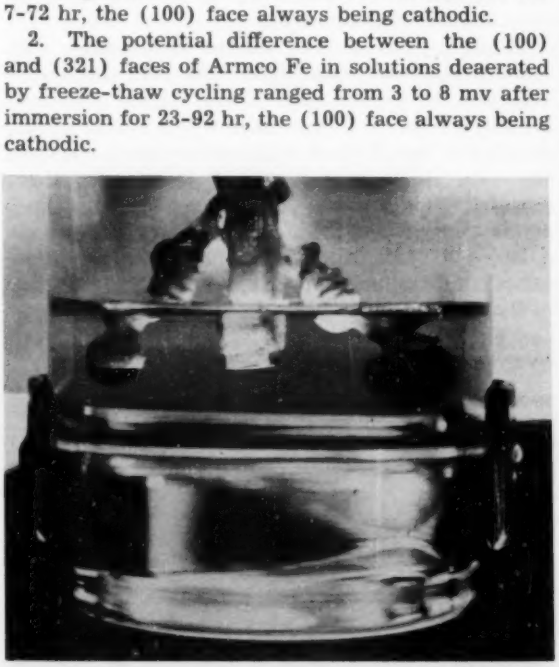

Fig. 5. Relative corrosion of the (321) face on the right and the (100) face on the left as indicated by the diffusion zone formed around the faces when connected to Sn and immersed in a citric acid gel containing potassium ferricyanide.

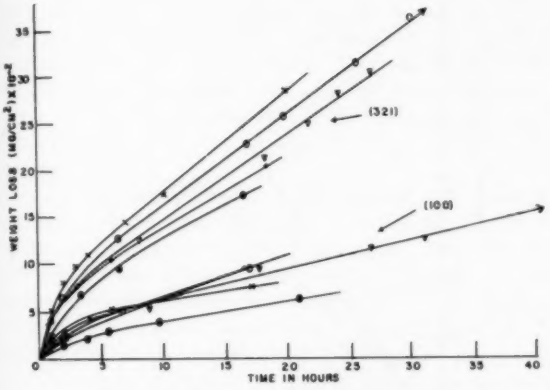

Fig. 6. Results obtained with single crystals of Armco Fe in experiments carried out at 20°C in 0.2M solutions of citric acid which had been deaerated by freeze-thaw cycling.

3. Both the (100) and (321) faces were cathodic to polycrystalline Sn in solutions deaerated by freeze-thaw cycling.

4. A potential difference existed between the (100) and (321) faces when all the exposed Fe except the flat crystal faces was coated with electrodeposited Sn and measurements were carried out in deaerated solutions. The (100)-Sn assembly was cathodic by 5-20 mv in exposures lasting up to 69 hr.

Quantitative Corrosion Measurements

Armco single crystals in deaerated 0.2M citric acid at 20°C.—Preliminary measurements were carried out on single crystals containing inclusions of one or two smaller crystals of unknown orientation. Results with these specimens were not reproducible and microscopic examination indicated that the irreproducibility could be attributed to the behavior of the grain boundary. In general, the boundary was attacked very rapidly both in the polishing operation before the start of a run and also during corrosion. The bond between neighboring crystals of Armco Fe, grown by the method described previously, is very weak as shown by the fact that often a ⅜ in. bar having two grains which cover the entire cross section can be readily broken by hand pressure.

Using crystals containing no inclusions, the results shown in Fig. 6 were obtained. For the linear portion of the curves the corrosion rate of the (100) face ranged from 0.0019 to 0.0044 mg/cm²/hr and averaged for the 5 runs, 0.0034 mg/cm²/hr. For the (321) face the rate ranged from 0.0078 to 0.0107 mg/cm²/hr and averaged 0.0091 mg/cm²/hr. Since the rates could be decreased slightly by additional freeze-thaw cycling there is reason to believe that the lack of better reproducibility was due to the presence of small amounts of air which were left after the 5 freeze-thaw operations.

Armco single crystals in deaerated 0.3N sulfuric acid at 20°C.—Three measurements were made in 0.3*N* H_2SO_4. The (100) face corroded at an average rate of 0.0091 mg/cm²/hr and the (321) corroded at 0.0168 mg/cm²/hr. These results are of minor significance since only a few measurements were performed, but they do show that the rate of corrosion of the (321) face is faster than that of the (100) face in H_2SO_4 as well as citric acid.

Table I. Rates of corrosion of the (100) and (321) faces of type L steel in boiling, refluxing 0.2M citric acid

Face	No. of mensurements	Corrosion rate in mg/cm²/hr Range	Average
	First Set		
(100)	4	0.7-1.3	1.0
(321)	7	3.1-6.0	4.8
	Second Set		
(100)	5	1.3-1.8	1.5
(321)	4	2.9-4.0	3.6
	Third Set		
(100)	3	1.8-2.1	2.0
(321)	3	3.7-4.2	4.0

Armco single crystals in boiling, refluxing 0.2M citric acid.—The average corrosion rate for the (100) face was 1.4 mg/cm²/hr and of the (321) face 3.0 mg/cm²/hr. (100) facets only were developed and a great deal of the corrosion of the (100) faces occurred by pitting. These pits (Fig. 3) had a square cross section and are confirming evidence that the corrosion of the (100) face occurred at the slowest rate.

Type L steel single crystals in boiling, refluxing 0.2M citric acid.—Three sets of specimens were used in these experiments. In the first set, disks exposing (100) and (321) faces were cut from a single large grain and in the two other sets the faces were cut from neighboring grains in a second slab. The results obtained with these specimens are summarized in Table I.

Corrosion of polycrystalline Armco iron in 0.2M citric acid at the boiling point.—The rate of corrosion of the original Armco Fe rods from which the single crystals were prepared ranged from 4.8 to 7.7 mg/cm²/hr with an average rate of 6.0 mg/cm²/hr. The grain size of this material was 560 grains/mm².

Corrosion of polycrystalline Armco Fe in 0.2M citric acid at the boiling point.—The 2½ in. x 2½ in. billets of L steel used to grow single crystals showed two distinctive regions when etched in HCl, a rim and a core section having a sharp boundary between them (*see* Fig. 1). A wet analysis of the rim and core millings yielded the following:[a]

	% C	% P	% Mn	% S
Core	0.089	0.018	0.29	0.059
Rim	0.038	0.011	0.25	0.024

Additional qualitative analyses confirmed that the concentrations of C, Mn, and S were higher in the core than in the rim section.

Corrosion rates of unannealed polycrystalline rim and core specimens were determined for comparison with one another and with single-crystal rates. The rim and core samples were machined in the shape of cylinders having their axes parallel to the rolling direction in the billet. A typical run is shown in Fig. 7 where results for single-crystal specimens are also given for comparison. In a series of experiments the rate of corrosion, as determined from the

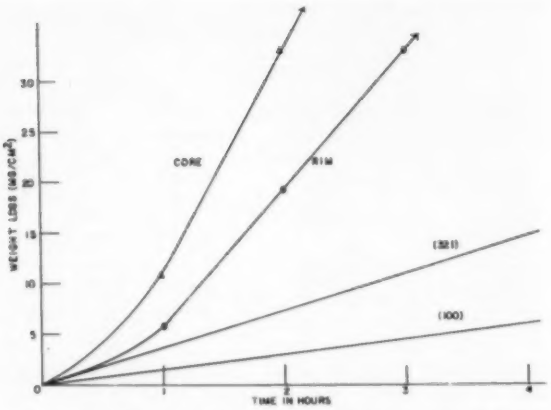

Fig. 7. Corrosion in 0.2M citric acid at the boiling point of polycrystalline samples cut from rim and core sections of the as-received billet. Rates of corrosion of single crystals prepared in the rim area are given for comparison.

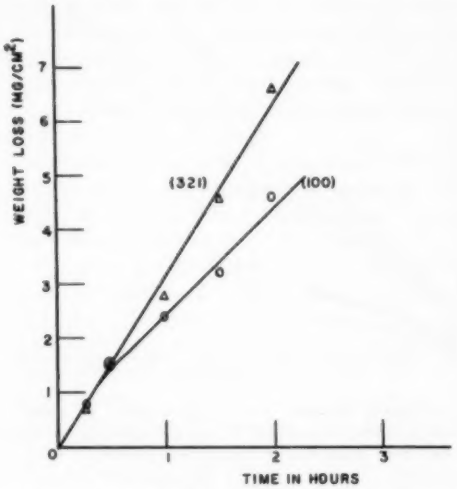

Fig. 8. Corrosion in 0.2M citric acid at the boiling point of single crystals of Armco Fe in the as-machined condition.

linear portion of the curve, ranged from 13.3 to 19.2 mg/cm²/hr for the rim and from 15.4 to 36 mg/cm²/hr for the core. The average values were 15.6 mg/cm²/hr for the rim and 26.6 mg/cm²/hr for the core.

A few experiments were also carried out on polycrystalline core specimens which were cut after the steel sample had been heated for 100 hr at an average pressure of approximately 50μ. The rates of corrosion of these specimens were in the same range as specimens which had not been subjected to any heat treatment.

Recrystallized Armco crystals in 0.2M citric acid at the boiling point.—In the first experiments, a disk exposing (100) faces and a disk exposing (321) faces were machined with a sharp lathe tool. The resulting surfaces yielded back-reflection x-ray patterns using Fe radiation indicative of fine-grained, polycrystalline iron. A typical corrosion experiment is shown in Fig. 8. The outstanding feature of this experiment is that the rate of corrosion of the machined (100) face was high at the start of the experiment and apparently was approximately the same as that of the machined (321) face. As the corrosion continued the rates diverged and assumed values of 1.7-1.9 mg/cm²/hr for the (100) face and 2.5-3.1 mg/cm²/hr for the (321) face. These values should be compared with values of the corrosion of the strain-free surfaces of 1.4 mg/cm²/hr for the (100) face and 3.0 mg/cm²/hr for the (321) face in experiments carried out immediately prior to the experiments in which the crystals were machined.

After 2 hr of corrosion, the surface of the (100) face had an appearance such as that shown in Fig. 9. When the crystal was examined with a flashlight, reflections were obtained only from one quadrant at a time. The photograph in Fig. 9 was taken with two light beams so that the 4 quadrants on the surface would be visible. Such a pattern on the surface presumably reflects the fourfold symmetry of the distortion of the crystal as it was cut in the lathe. The fact that only one quadrant at a time reflected light from the flashlight suggests that at the completion of the experiment the (100) planes in the surface layers were not parallel to the surface. Some distortion still existed in the surface layers.

Recrystallization of a disk exposing (100) faces and a disk exposing (321) faces was carried out by heating the disks in vacuum to 1000°C and cooling slowly. The phase change from the low temperature body-centered cubic structure to the high temperature face-centered cubic structure on heating and the reverse change on cooling resulted in recrystallization. The grain size obtained after slow cooling to room temperature was 42 grains/mm² on both specimens. Metallographic examination showed a striking substructure within many of the grains.

The average rate of corrosion of the recrystallized (100) disk was 4.4 mg/cm²/hr and of the recrystallized (321) disk was 4.1 mg/cm²/hr on samples polished in Mirro-Fe. In one experiment carried out on specimens which had been surfaced by machining with a sharp lathe tool, the rates of corrosion were 4.8 and 4.6 mg/cm²/hr for the recrystallized (100) and (321) disks, respectively.

Recrystallized type L steel crystals in 0.2M citric acid at the boiling point.—A disk exposing (100) faces and a disk exposing (321) faces were recrys-

Fig. 9. Pattern on the surface of a machined (100) disk after corrosion for 2 hr in 0.2M citric acid at the boiling point.

tallized in the same manner as the Armco crystals by heating them to 1000°C in vacuum and cooling slowly to room temperature. A grain size of 48 grains/mm² resulted. The average rate of corrosion of the recrystallized (100) disk was 5.3 mg/cm²/hr and of the recrystallized (321) disk was 5.5 mg/cm²/hr.

In a second series of experiments, the recrystallized (100) was strained by compressing it so that the thickness was decreased to 75% of its former value. The average rate of corrosion of this recrystallized and strained disk was 3.5 mg/cm²/hr.

In order to obtain preliminary information useful in a future thorough study of the effect of grain size on corrosion rate, the following experiments were performed. The recrystallized and strained (100) disk resulting from the experiments with the compressed specimen and the recrystallized (321) disk were converted to fine-grained specimens by heating them to 1000° and quenching them in cold water. Grain sizes in these specimens were 1550 and 1600 grains/mm². The rates of corrosion of these specimens ranged from 7.1 to 8.5 and averaged 7.9 mg/cm²/hr.

Corrosion in the presence of dissolved Sn(II) *ions.*—Preliminary experiments were carried out in an attempt to determine the relative amounts of Sn and single-crystal Fe which corroded when the two materials were in good contact and equal areas of both metals were exposed to the solution. These experiments indicated that the presence of Sn decreased greatly the corrosion of the steel. The purpose of the next experiments was to attempt to separate effects due to galvanic action from effects due to inhibition by dissolved Sn(II) ions.

In order to avoid the introduction of other ions into the solution, the Sn(II) was added to the citric acid solutions by corroding a piece of Sn wire in the acid. The Sn wire corroded in the boiling, refluxing 0.2M citric acid at a rate of 0.0071 mg/cm²/hr and an accuracy of 1 part in 40 could be obtained by corroding a Sn wire of known surface area for a known period of time. The results of the experiments can be summarized in the following three statements:

1. There was no difference in behavior of the (100) and (321) faces.

2. In the presence of 40 ppm of Sn(II) the average rate of corrosion at the boiling point was 0.04 mg/cm²/hr for exposure times up to 11 hr.

3. In the presence of 43 ppm of Sn(II) the average rate of corrosion in deaerated solutions at 20°C was 0.001 mg/cm²/hr for exposure times up to 2160 hr.

In the earliest experiments Sn(II) was introduced by dissolving SnO in the citric acid solution. In these experiments the average rate of corrosion of the (100) face was 2.1 mg/cm²/hr and the average rate of corrosion of the (321) face was 2.5 mg/cm²/hr. The rate of corrosion of the (100) face was apparently unaffected by the addition of Sn(II) ions, whereas the rate of corrosion of the (321) face was appreciably reduced. The concentration of Sn(II) in solution in these experiments was unknown because of incomplete solutions of the SnO, but was less than 11.5 ppm.

Discussion

Seven different types of experiments reported herein indicate that in the acids studied the (100) face corrodes at a slower rate than the minor faces of which the (321) face is an example. These seven types are: (*a*) reaction patterns on the spheres; (*b*) experiments in the citric acid gel; (*c*) potential measurements; (*d*) rates of hydrogen evolution from crystals exposed to deaerated citric and sulfuric acids; (*e*) corrosion in boiling 0.2M citric acid; (*f*) observations of the individual grains in polycrystalline steel; and (*g*) formation of facets and etch pits exposing (100) faces during corrosion in 0.2M citric acid.

On the basis of these observations there can be no doubt that the (100) corrodes at a slower rate and the (321) at a much more rapid rate in 0.2M citric acid. The question that still remains to be answered is why does this difference exist. Since (100) facets are developed on both the (100) face and the (321) face during corrosion there is the possibility that the relative rates may be correlated with the relative amounts of (100) surface exposed on the two faces. On the other hand, Fe atoms exposed at the joining edge of a (100) and (010) facet, for example, would be expected to be more vulnerable to attack by the acid. The relative rates of corrosion might be correlated with the relative amount of edge area exposed on the (100) and (321) faces. With the experimental data available at present it is not desired to express a preference for either of these or other possible explanations of the results. Regardless of the explanation of the results, the very fact that (100) facets are formed indicates that the (100) and (321) faces have different inherent rates of corrosion.

The possibility that the method of surface preparation controls the relative rates of reaction is ruled out by the fact that similar relative rates were obtained on (100) and (321) surfaces that were: (*a*) chemically polished in Mirro-Fe, (*b*) electrolytically polished, (*c*) machined, and (*d*) polished with emery paper. Of course in the latter two cases, the rates only approached the rates of the strain-free specimens, when the heavily strained outer layers had been removed in the corrosion process.

Potential measurements show that the (100) face is cathodic to the (321) face in citric acid. Potential measurements and rate measurements thus support one another. The cathodic nature of a grain exposing a (100) face relative to a neighboring grain exposing another type of face was observed many times in microscopic observations of polycrystalline aggregates. These observations confirm the view that some types of corrosion may have their origin in the potential difference between the crystal faces on the grains exposed at the surface.

The etch pattern obtained in the acids and shown in Fig. 2 indicated, on the basis of the rate of roughening, that the rates of corrosion of the minor faces surrounding the (111) pole position were much

Table II. Summary of important results on the corrosion rates in 0.2M citric acid at the boiling point

	Armco		Type L	
	(100)	(321)	(100)	(321)
	(all values in mg/cm²/hr)			
Starting material from which single crystals were prepared	4.8-7.1		13.3-19.2 (rim) 15.4-36 (core)	
Chemically polished single crystal	1.4	3.0	1.0-2.0	3.6-4.8
Machined crystal (start of corrosion)	2.2-3.0	2.8	——	——
(after reaching linear rate)	1.7-1.9	2.5-3.1	——	——
Recrystallized to 42-48 grains/mm² (chemically polished)	4.4	4.1	5.3	5.5
Recrystallized to 42 grains/mm² (machined surface)	4.8	4.6	——	——
Recrystallized to 1550-1600 grains/mm² by quenching from 1000°	——	——	7.1-8.5	
In the presence of 40-45 ppm [Sn(II)] (chemically polished)	——	——	0.03-0.1	0.02-0.07

more rapid than the (100) and the minor faces surrounding this plane. This type of surface pattern on electrolytically polished cubic single crystals is often observed and such patterns have been described for the formation of carbonaceous deposits on Cu single crystals immersed in aviation oil (10), the etching of Cu crystals in a $CuSO_4$-H_2SO_4 electrolyte (11), the deposition of C from the decomposition of CO on single crystals of Ni and Co (4), and the formation of free Ag during the photographic development of single crystals of AgCl (3). This same type of pattern has been observed many other times in unpublished experiments. This commonly observed pattern is confirming evidence for the view that the crystal planes making small angles with the (111) plane are unstable.

The corrosion studies which were carried out in 0.2M citric acid at the boiling point are summarized in Table II. Several of the important results are now discussed.

In the case of both the Armco and L-steel single crystals, the corrosion rate was apparently less than that of the starting material from which the single crystals were prepared. Significant reduction in C concentration only took place during the growth of the single crystals of L-steel as shown by the following analyses of single crystals of steel prepared from a different billet than was used in the corrosion studies.[a]

The reduced rate of corrosion of the single crystals may be accounted for in part by the reduction in C concentration, since C is known to increase the rates of corrosion of steels by fruit acids (12). That this purification is not the complete explanation is shown by the results obtained with the recrystallized single crystals. In the case of single crystals recrystallized to yield a grain size of 42-48 grains/mm² the corrosion rate of the (100) face was increased greatly and the rate of the (321) was increased appreciably, but much less than the (100). When these same crystals were recrystallized by heat treatment to a grain size of 1550-1600 grains/mm², the rate increased to an average rate of 7.9 mg/cm²/hr. Although this latter grain size is much smaller than the as-received material, the rate of corrosion is appreciably less, emphasizing the importance of both purity and grain size.

These results all point to the conclusion that the presence of grain boundaries results in a higher corrosion rate. Judging from the square pits formed on the surface of some of the grains, there was an appreciable concentration of grains whose (100) planes were oriented approximately parallel to the surface. It would be expected then, in the absence of grain boundary effects or the effect of one grain on another, that the corrosion rate of polycrystalline iron or steel would be between the low rate of the (100) face and the high rate of the (321) face.

It is generally recognized that Sn(II) ions decrease the rate of corrosion of steel in deaerated fruit acids (13-15), but the discovery made in this research is that the Sn ions had the ability to make the corrosion rate of the (100) and (321) faces the same. The apparent uniform activity of the faces was dramatically illustrated in experiments with spheres. When a single crystal sphere was immersed for two weeks in boiling, refluxing 0.2M citric acid containing 50 ppm of Sn(II), no corrosion

	Si	Mn	Mo	Cr	Cu	Ni	C	P	S
Starting material (rim)	0.005	0.36	<0.002	<0.012	0.024	0.013	0.035	0.016	0.025
Starting material (core)	0.005	0.35	<0.002	<0.012	0.020	0.018	0.042	0.028	0.022
#1 Crystal (rim)	0.005	0.29	<0.002	<0.012	0.023	0.012	0.017	0.016	——
#2 Crystal (rim)	0.012	0.36	<0.002	<0.012	0.038	0.012	0.020	0.022	——
#2 Crystal (core)	0.009	0.32	<0.003	<0.012	0.024	0.011	0.014	0.032	——
#3 Crystal (rim)									0.027
#3 Crystal (core)									0.047
#4 Crystal (rim)							0.006		
#4 Crystal (core)							0.014		

Crystals bearing the same number occupied both the rim and the core. Before analysis they were cut along the boundary between the rim and the core.

pattern formed on the sphere. In another experiment terminated at the end of 8 hr in 0.2M citric acid containing 10 ppm Sn(II), no pattern was observed. In these experiments with the spheres there was some localized pitting which did not appear to be related to crystal orientation, but the highly polished surface was retained until the end of the experiment.

In experiments carried out with single crystals at the boiling point in 0.2M citric acid containing approximately 40 ppm of Sn(II) no Sn or Sn compounds could be detected on the surface by either electron diffraction examination or by visual observation. The electron diffraction patterns showed lines due to iron oxide as would be expected. In runs with polycrystalline steel specimens and carried out for 96 hr, visible signs of Sn were detected on the surface. This experiment indicates that there is a tendency for stannous ions to be converted to metallic tin on a steel surface under the conditions used.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1958 JOURNAL.

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Kinetic Studies on Formation of Black-Oxide Coatings on Mild Steel in Alkaline Nitrite Solutions

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ABSTRACT

The formation of black-oxide (magnetite) coatings on mild steel in hot concentrated solutions of sodium hydroxide and sodium nitrite was studied over the temperature range 130°-150°C. The following mechanism is proposed for the over-all reaction:

$$Fe \xrightarrow[OH^-]{NO_2^-} Fe(OH)_2 \qquad [1]$$

$$Fe(OH)_2 \xrightarrow[OH^-]{NO_2^-} Fe(OH)_3 \rightleftarrows FeO_2^- \qquad [2]$$

$$Fe(OH)_3 \rightleftarrows Fe^{+++} + 2\,OH^- \qquad [2a]$$

$$Fe^{+++} + 2\,FeO_2^- \rightarrow Fe(FeO_2)_2 \qquad [3]$$

Of the total iron dissolved in step [1], only about 30% was converted to black oxide on the surface. Values of the rate constant for step [1] were obtained from plots of total iron dissolved vs. time. Plots of the initial rates (oxide-free surface) vs. 1/T were linear, with an energy term of 41 kcal/mole. As the oxide coating built up, the rates dropped to a fraction of the initial rate and the energy term increased sharply. For thicker films the rates are apparently controlled by diffusion of the reactants through the film.

Alkaline oxidizing baths are used in the metal finishing industry to form black-oxide coatings on ferrous metals, particularly mild steels. All of the proprietary baths generally use the same process conditions and salt compositions. The principal ingredients are a strong alkali, usually NaOH, and an oxidizing agent, $NaNO_2$ or $NaNO_3$, or a mixture of these two. Proportions vary somewhat from bath to bath, and some contain small amounts of addition agents, although the effectiveness of these agents has not been clearly demonstrated.

The advantages and limitations of the black-oxide coatings have been described previously (1). Briefly, they provide some additional resistance to atmospheric corrosion, but fail rapidly in salt spray tests and at high humidities. Oxide-coated pieces are usually given additional protection by use of a supplemental oil film, formed by immersion in a hot soluble oil bath (2). This treatment not only imparts a considerable increase in corrosion resistance, but also enhances the decorative value of the oxide coat.

It is believed that the low resistance of the oxide-coated steel without the supplemental oil film is due to the slight porosity and to the thinness (in the order of a micron) of the coatings. The purpose of the research described in this paper was to study the chemical processes and mechanisms involved in the oxide formation.

Experimental

The salts used in all experiments were furnished by the Eltex Chemical Corporation of Providence, Rhode Island, and were of the usual commercial grade. The composition of the salts was about 66% NaOH and 33% $NaNO_2$. The baths were prepared by adding 1000 g of the salt mixture to sufficient water to adjust the boiling point of the solution to any desired operating temperature in the range 130°-150°C. The bath temperature was controlled by operating the bath at the boiling point and adding make-up water at a rate equivalent to that lost by evaporation. The baths were contained in a large Pyrex beaker, which resulted in the accumulation of small quantities of silicates in the solution. However, the effect of silicates, if any, was minimized by preparing a fresh bath for each run, and by repeating the initial point after the completion of each run.

Coupons were cut to approximately one inch square from 0.010 in. mild steel (SAE 1045) shim stock, and were finished by sanding lightly with 3/0 emery paper. The coupons were immersed in the bath for periods ranging from 0.5 to 15 min, after which they were removed and immediately quenched in cold water. After the weight loss, of the order of a few milligrams, was obtained, the oxide coating was removed by immersing the coupons for a few seconds in 20% HCl, and again recording the weight loss. From these two weight losses, it was determined that only about 30% of the total iron dissolved appeared in the oxide coat, the remainder being lost to the solution.

Each point in the figures represents an average of data taken on three coupons, except for the run at 134°C. For some reason, considerable difficulty

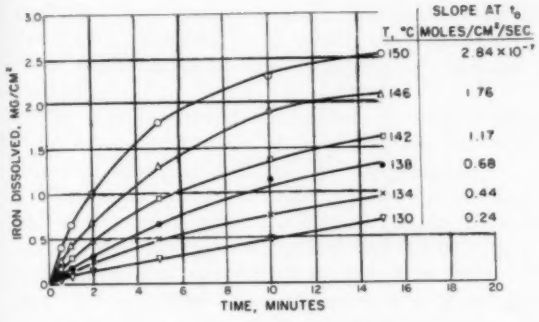

Fig. 1. Total iron dissolved at various temperatures

was encountered in obtaining reproducible weight losses at this particular temperature; the points shown were obtained by averaging data from nine coupons at each time. At the other temperatures, weight losses generally were reproducible to within less than 2.0%.

Results

The total iron dissolved by the oxidizing bath was obtained by adding the two weight losses obtained as described above. These data are shown plotted against time in the bath in Fig. 1 and 2. Fig. 1 shows that the iron dissolution reaction rate decreases markedly as the oxide film builds up. At the lower temperatures, where the film forms more slowly, the decrease is less than at the higher temperatures. As a matter of fact, the slopes of all of these curves after 15 min in the bath are approximately equal at all temperatures, while the initial rates vary over an order of magnitude. Fig. 2 shows that a log-log plot gives a family of straight lines of approximately equal slopes. The values of $d(\mathrm{Fe})/dt$ for Fig. 3 and 5 were obtained by replotting these straight lines on an expanded linear scale through the time interval desired.

In removing the oxide film, it was noted that dissolution occurred first at the corners and edges of the coupon, and then progressed very rapidly toward the center. Also there was no tendency for the steel itself to be attacked by the acid until some 2 or 3 min after the black-oxide had disappeared. This suggests that a very thin (passivating?) film remains on the surface during this period. No detectable weight loss was observed during the interval after the film was removed and before the metal was visibly attacked.

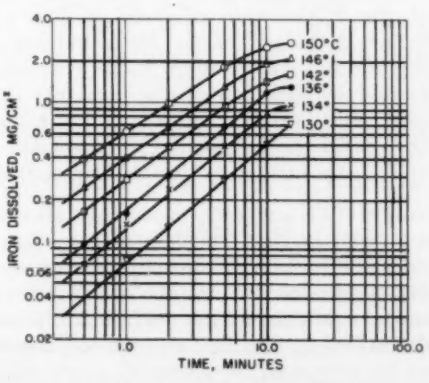

Fig. 2. Log-log plot of data of Fig. 1

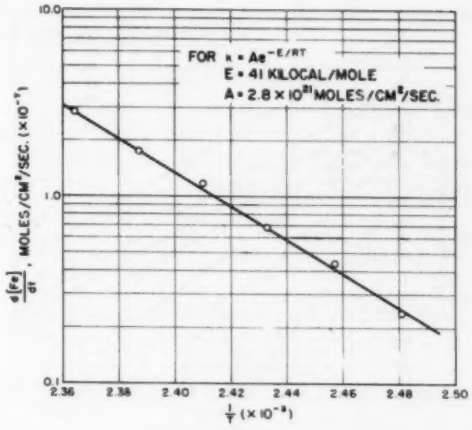

Fig. 3. Arrhenius plot of initial rate constants

In Fig. 3 the initial slopes of the curves of Fig. 1 are plotted against the reciprocal of absolute temperature. It is assumed that in the initial stage of the reaction, the rate of iron dissolution is described by:

$$\frac{d(\mathrm{Fe})}{dt} = k(X) \qquad (I)$$

where X is the fraction of the total surface available for the reaction. For Fig. 3, the slopes are taken at $t = 0$, where $X = 1.0$. A typical Arrhenius plot is obtained, with an energy of activation of 41 kcal/mole and a frequency factor of 2.8 x 10^{21} moles/cm²/sec.

The thickness of the oxide film was estimated by dividing the weight of film per square centimeter by the bulk density of magnetite, $Fe(FeO_2)_2$. While there is no evidence to show that the black-oxide is 100% magnetite, portions of the film removed intact exhibit ferromagnetism. It should be pointed out that, at temperatures only slightly above 150°C, the film contains visible amounts of reddish-yellow oxide, and is presumably a mixture of magnetite and ferric oxide. While it is possible that small amounts of ferric oxide (not visible) may be present at 150°, or even 146°, they are not likely to be significant, and the estimates of film thicknesses as

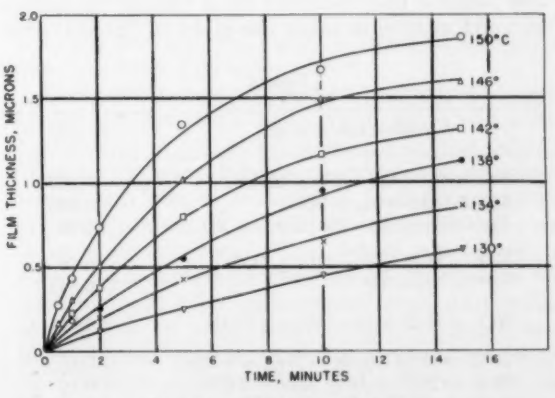

Fig. 4. Growth of film thickness

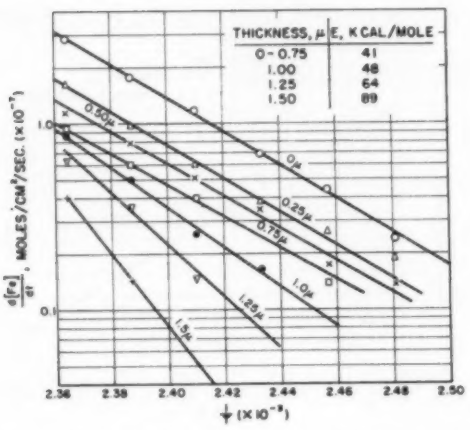

Fig. 5. Arrhenius plot of rate constants at different film thicknesses

plotted in Fig. 4 are reasonably accurate. The thickest film obtained after 15-min immersion at 150° was 1.85μ. It is interesting to note that, since only some 30% of the total iron dissolved goes into the film, there is actually a very slight decrease in the dimensions of steel pieces when treated in these baths, although the changes are so small as to be negligible in most cases.

For each temperature, the times at which the films build up to a given thickness can be read from Fig. 4. By taking the slopes of the curves in Fig. 1 at these times, the curves of Fig. 5 were obtained. Although the data do not fall on such well-defined straight lines as those of Fig. 3, it is clear that no significant change in the energy term for the iron dissolution reaction occurs until the film has built up to a thickness of at least 0.75μ. As the film thickens beyond this point, the energy term increases sharply.

Mechanism and Reactions

The determination of the exact oxidation reactions which occur in these baths is complicated by the fact that the standard oxidation-reduction potentials for the possible half-cell reactions are not known at these temperatures. Furthermore, the numerous reactions possible with the oxides of nitrogen, the nitrates and nitrites, and the equilibria between them are additional complicating factors. The possible half-reactions for a system containing iron and nitrites in alkali are given in Table I, with

Table I.

Possible half-reactions	E_0, volts
$Fe(OH)_2 + 2e \rightarrow Fe + 2OH^-$	−0.877
$2H_2O + 2e \rightarrow H_2 + 2OH^-$	−0.828
$Fe(OH)_3 + 1e \rightarrow Fe(OH)_2 + OH^-$	−0.56
$NO_3^- + H_2O + e \rightarrow NO + 2OH^-$	−0.46
$Fe^{++} + 2e \rightarrow Fe$	−0.441
$NO_3^- + H_2O + 2e \rightarrow NO_2^- + 2\,OH^-$	+0.01
$2NO_3^- + 3H_2O + 4e \rightarrow N_2O + 6\,OH^-$	+0.15
$2NO + H_2O + 2e \rightarrow N_2O + 2\,OH^-$	+0.76
$FeO_4^- + 4H_2O + 3e \rightarrow Fe(OH)_3 + 5OH^-$	+0.90

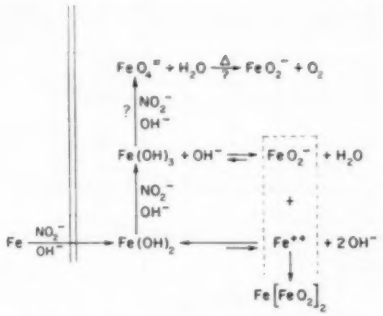

Fig. 6. Proposed mechanisms of black-oxide formation

their standard reduction potentials at 25°C, as given by Latimer and Hildebrand (3). If it is assumed that the reactions maintain approximately the same relative positions as the temperature is raised into the 130°-150°C range, then the probable net oxidation reactions are:

$$2Fe + 2NO_2^- + 3H_2O \rightarrow 2Fe(OH)_2 + 2OH^- + N_2O \quad (II)$$

$$4Fe(OH)_2 + 2NO_3^- + 3H_2O \rightarrow 4Fe(OH)_3 + N_2O + 2OH^- \quad (III)$$

According to these reactions, the gas evolved when steel is immersed in the baths should be predominantly N_2O. An effort was made to collect and analyze some of the gas, but because of the difficulties involved in carrying out such an experiment on these hot caustic solutions, it was abandoned with inconclusive results.

The last half-reaction given in Table I, the oxidation of $Fe(OH)_3$ to ferrate, is presented because there is some evidence that small amounts of ferrates are formed at the higher temperatures. The characteristic purplish-red color of the ferrates was observed momentarily in the layer of solution on the steel surface after quenching. Also, if the coupon is made sufficiently anodic (by an electrical circuit) in these solutions, a heavy purple-red streaming occurs which dissipates slowly, apparently due to the decomposition of the unstable ferrate into the colorless ferrite. A standard method of making alkali ferrates is by fusion of nitrite with $Fe(OH)_3$ (4), so that it is not unreasonable to assume that small amounts of ferrates are formed in these solutions near 150°C.

The probable over-all mechanism for the formation of the black-oxide is given in Fig. 6. The double line at the left of the figure indicates that, after the film has started to form, the reaction must be preceded by diffusion of the reactants through the oxide. The $Fe(OH)_2$ formed in the initial step must then yield the ferrous ion by dissociation and the $Fe(OH)_3$ by further oxidation. The equilibrium between $Fe(OH)_3$ and FeO_2^- in strongly alkaline solutions is well known. The loss to the solution of a considerable portion of the total iron dissolved is probably accounted for by the small amount of ferrous ion available at the surface for precipitation of $Fe(FeO_2)_2$. The low ferrous ion concentration can be accounted for either by a low solubility of $Fe(OH)_2$, or by a very rapid oxidation to

$Fe(OH)_3$. Apparently, as only 30% of the total iron appears as $Fe(FeO_2)_3$, of which only one-third is Fe^{++}, about 90% of the $Fe(OH)_2$ is oxidized to $Fe(OH)_3$.

The formation and subsequent decomposition of the ferrates are indicated in the figure, but with a question mark to indicate the uncertainty.

The kinetics of the over-all mechanism are almost certainly controlled by the initial reaction. It is suggested that for film thicknesses up to about 0.75 μ, this reaction is controlled by Eq. (I), where $k = Ae^{-41,000/RT}$ and $X = 1.0$ at thickness 0 μ, $X = 0.55$ at thickness 0.25 μ, $X = 0.42$ at thickness 0.50 μ, $X = 0.30$ at thickness 0.75 μ.

As the thickness increases beyond 0.75 μ, the change in the energy term reflects the increasing importance of diffusion through the layer in controlling the rate. This means essentially that the film is porous, but that the porosity decreases as the film thickens. Presumably, if thick enough films could be produced, the process would be entirely diffusion-controlled, and the energy term in Eq. (I) would become constant again at some value greater than 89 kcal/mole.

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Annealing Anodic Ta_2O_5 Films

Changes in Dissolution Behavior and X-Ray Scattering

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ABSTRACT

Upon annealing anodic Ta_2O_5 films the rate of solution of the film in HF decreases and the x-ray diffraction pattern from the film becomes sharper. The activation energy for the process responsible for changes in solution rate is approximately the same as those observed for changes in ionic conduction upon annealing and for ionic conduction itself. It is believed that changes in local ionic configuration are the cause of these property changes. The rate at which these changes occur appears to be controlled by the rate of tantalum ion motion.

Annealing anodic Ta_2O_5 films results in a decrease in their ionic conductivity. This decrease has been interpreted (1) in terms of a mechanism involving changes in the local ionic configuration, perhaps similar to the changes which are known to occur in glasses upon annealing. In this paper the changes in the rate of solution of the film in HF and the changes in scattering of x-rays which accompany annealing are discussed. A comparison of the activation energies involved indicates that ionic conductivity and changes in ionic conductivity and dissolution behavior may all be controlled by the same process, which is probably Ta ion migration.

Experimental

X-Ray Diffraction Studies

It was found by Hillig (2) that oxide films formed on chemically polished[1] Ta specimens could easily be stripped intact from the metal by the following procedure. A layer of nitrocellulose was applied to the surface of the oxide film from a solution of 10% nitrocellulose in amyl acetate. The edges of the coupon (¼ in. x 2 in.) were scraped with a razor blade to prevent continuity of the oxide and the nitrocellulose film around the edge. The nitrocellulose film was then carefully lifted off the specimen; the oxide film came with it.

X-ray diffraction specimens consisted of several layers of films about 3000Å thick formed in 0.2% Na_2SO_4 at room temperature using a current density of about 2 ma/cm^2. Films were stripped as described above, cut into ¼ in. squares, and placed nitrocellulose side up on a small Pt holder having a ⅛ in. hole in the center. This holder was placed in a spot plate containing ethyl acetate to dissolve the nitrocellulose. After at least four separate rinsings of the film in ethyl acetate another square was placed on top and the nitrocellulose dissolved away. This process was repeated until there were six thicknesses of oxide film (about 2μ) on the holder.

[1] Polishing solution: 55% H_2SO_4 (96%), 25% HNO_3 (70%), and 20% HF (48%) by volume.

Diffraction patterns of films heated 2 min at various temperatures were taken using Cr Kα radiation in a cylindrical camera of 10 cm diameter using a He atmosphere to reduce low angle scattering by air. The radiation was not made truly monochromatic by diffraction from a crystal because the small sample thickness would have required very long exposure times. A L&N microphotometer was used to obtain a curve of intensity vs. distance on the film. Crystalline Ta_2O_5 gives a diffraction pattern with two strong lines at $d = 2.44$ and $d = 3.14$ and a somewhat weaker one at $d = 3.9$; in the amorphous material these three lines contribute to one broad halo. The main contribution, however, is from the stronger lines at $d = 2.44$ and 3.14. In order to separate the lines it was necessary to find three symmetrical Gaussian curves which when added together gave the observed pattern (corrected for background). The breadths of the two highest Gaussian curves were then measured at half height and the result used as a measure of the diffuseness of the pattern. A pattern was also taken for a 0.001 cm flake of fused quartz for comparison with the Ta_2O_5 patterns.

Dissolution Studies

If a Ta_2O_5 film on the Ta electrode on which it was formed is dipped into 48% HF it will dissolve slowly and uniformly (3), so that changes in thickness can be measured by comparison with an optical step gauge (4). However, HF changes strength rather rapidly on standing and in use, so that some method of calibrating the dissolving power of the solution was required. The method used was to dissolve a series of films in which every third film was one formed in a standard manner, the others having been annealed. A plot of the rate of solution of the standard film vs. the test number was used to find by interpolation the solution rate of a standard film at any test. The solution rate of the standard film was taken arbitrarily as 20Å/sec, and all test results on annealed films were multiplied by the ratio of 20Å/sec to the interpolated solution rate of the standard specimen for that test. The solution rate obtained for the annealed specimen was thus the rate of solution relative to that of the standard film.

All of the films were formed by anodization at 1.56 ma/cm^2, 29°C, to 120 v using a 1% Na_2SO_4 electrolytic solution. The film thickness produced was 1759Å ± 10Å. After formation the films were annealed on the Ta electrode at different temperatures using baths of water, silicone oil, molten lead-bismuth-tin alloy, molten KCl-LiCl mixture, or air depending on the time and temperature. Results were the same regardless of the method of heating at temperatures up to 330°C. The standard films were formed in exactly the same manner but were not annealed.

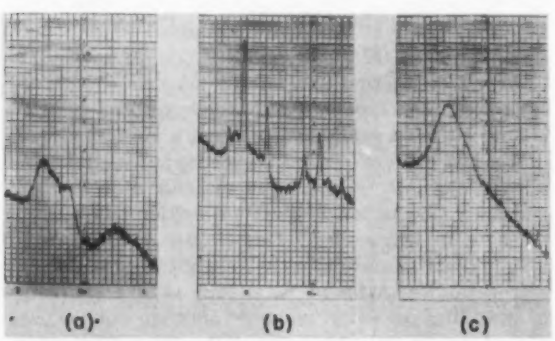

Fig. 1. Diffraction intensity vs. diffraction angle: (a) an anodic Ta_2O_5 film heated 2 min at 555°C; (b) same at 750°C; (c) for vitreous silica.

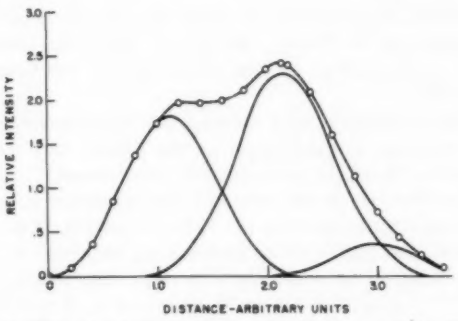

Fig. 2. Diffraction intensity (corrected for background) vs. diffraction angle, showing the resolution of the broad diffraction maximum into its three component maxima.

Experimental Results

X-Ray Diffraction Studies

Fig. 1 shows microphotometer traces of an amorphous Ta_2O_5 film, crystalline Ta_2O_5 film, and quartz, respectively. The patterns for quartz and amorphous oxide are qualitatively similar, showing very broad halos and considerable small angle scattering [the small angle scattering is probably a result of the technique used, since Warren (5) found little small angle scattering from quartz]. It seems not unreasonable, therefore, that the anodic films have a glassy structure. The peaks in the pattern for crystalline Ta_2O_5 appear at about the same position as do the maxima in the amorphous pattern.

Fig. 2 is a replot of the data from one of the microphotometer traces from which the background has been subtracted, and shows how the three Gaussian curves have been added to give the observed curve. The values of line breadths from experiments using two separate specimens are given in Table I. The time of annealing at each temperature was 5 min.

There is a definite decrease in line breadths for both films; the decrease is greater for film No. 1. The two

Table I. Values of line breadths

Film No.	Annealing temp, °C	Line breadth at half height arbitrary units
1	As formed	1.03
	210	0.93
	375	0.90
	555	0.83
2	As formed	0.92
	108	0.91
	210	0.89
	338	0.84
	505	0.83
	620	0.82

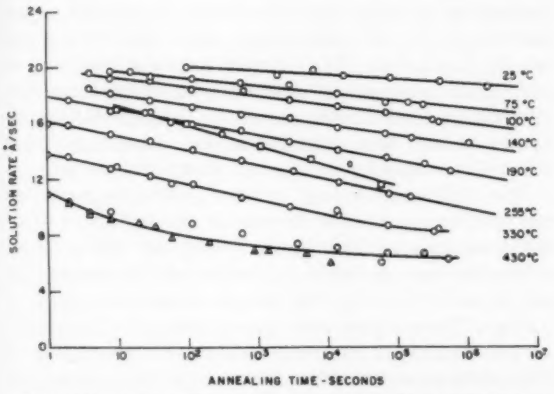

Fig. 3. Change of relative solution rate with time of annealing at various temperatures. For the 430°C anneal the circles denote that the films were heated in air while the triangles denote films heated in molten KCl-LiCl mixture. The squares are used for the data obtained when films were held at 140°C with an applied electric field of 0.029 v/Å (curve a).

films were made at the same time and in exactly the same way, so they should have been identical. However, about a month elapsed between the two sets of experiments, and the fact that the original pattern for film No. 2 was less diffuse may be the result of annealing for one month at room temperature.

No attempt was made to determine the exact structure of these films from the x-ray data. A very rough indication of the extent of local order can be obtained from the particle size which would be necessary to cause such line broadening. This does not imply that such particles exist but, if the diffuse pattern were the result of a very small particle size, the order of magnitude of the mean particle diameter would be about 10Å. Because of the qualitative similarity between the patterns for the Ta_2O_5 films and those obtained from vitreous quartz, the simplest interpretation of the x-ray data is that the anodic films have a glass-like structure, and that changes in the local configuration on annealing the film result in a sharper x-ray pattern.

Dissolution Studies

The rate of solution of annealed oxide films decreases nearly linearly with the logarithm of the time of annealing at temperatures from room temperature to 330°C (Fig. 3). At 430°C the solution rate appears to be approaching a minimum after about 10^5 sec, and the results are slightly different depending on whether the specimens were heated in air or in molten KCl-LiCl mixture. The results of transient studies on films heated at high temperatures (6) indicate that oxygen mobility in the oxide becomes appreciable above about 350°C, and that some solution of oxygen in the Ta occurs, particularly at grain boundaries. The different behavior at 430° and the dependence on atmosphere are probably associated with this increased oxygen mobility.

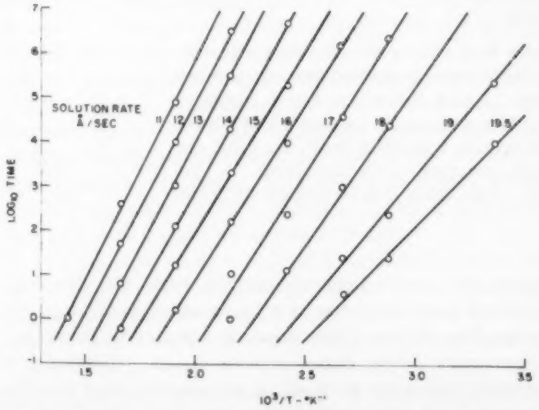

Fig. 4. Logarithm of the time required to reach a designated solution rate vs. the reciprocal of the temperature.

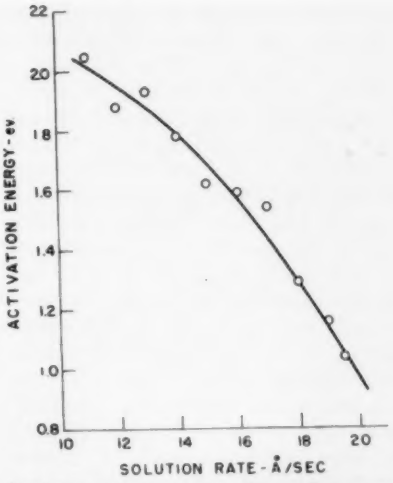

Fig. 5. Activation energy vs. extent of annealing as measured by solution rate.

A plot of the logarithm of the annealing time required to reach a particular solution rate vs. $1/T$ is shown in Fig. 4, and the activation energy determined from the slopes of these curves vs. solution rate is shown in Fig. 5. The activation energy increases from about 1 ev to 2 ev as the solution rate decreases from 20 to 11.

The dependence of the solution rate on time of annealing at 140°C is shown in Fig. 6 for films having three different histories. The solution rate is plotted against log (time at 140°C plus 3700 sec) in curve 2 since the initial solution rate for these films (16.2Å/sec) would have been produced in 3700 sec at 140°C, and against log (time at 140°C plus

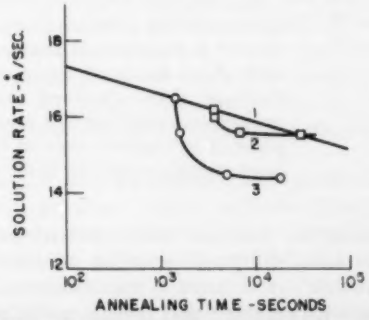

Fig. 6. History effect in annealing. Curve 1 is the same as that for 140°C from Fig. 3. Curves 2 and 3 are for films heated at 140°C after holding for 100 sec at 190°C, and at 80°C with an applied field of 0.055 v/Å, respectively.

1400 sec in curve 3. These results show clearly that a given solution rate does not completely describe the state of the film, since the behavior upon annealing at 140°C depends on film history.

It should be noted that the same solution rate is produced by holding a film at 140°C for 1400 sec or at 80°C with a field of 0.055 v/Å. Thus, annealing with an applied field results in a more rapid change in the solution rate. This is also shown very clearly in Fig. 3, curve a, which was obtained for films held at 140°C with an applied field of 0.029 v/Å. Solution rates are roughly comparable to those obtained upon annealing at 190°C with no field applied.

In addition to changes in the solution rate produced by annealing the film with or without an applied field, changes in the solution rate also occur if the rate of film formation is changed at one temperature. At room temperature, for example, the solution rates were 19.3Å/sec, 20Å/sec, and 20.3Å/sec, after formation at rates of 0.4Å/sec, 8Å/sec, and 40Å/sec, respectively. While these changes are small and probably would make observation of any change in x-ray scattering extremely difficult, it seems reasonable to expect that such changes do occur, and that the same kind of change in film structure which occurs on annealing also occurs on changing the rate of film growth.

Discussion

According to the mechanism proposed previously[1], the passage of a large ionic current through a Ta_2O_5 film results in changes in local configuration which facilitate conduction. Upon annealing, or upon formation at a lower electric field, the structure changes toward a new configuration. X-ray data clearly indicate that some kind of change in the direction of increased order does occur upon annealing. The dissolution data show an increased chemical stability of the film, which would be expected on intuitive grounds if the structural order increased. It is interesting that the crystalline anodic Ta_2O_5 film (7) is almost entirely resistant to HF. Upon attempting to dissolve a crystalline film no change in film thickness occurs, but the HF penetrates under the crystallites and separates them from the metal by dissolving away the metal.

The activation energy for the process responsible for the change in solution rate is about 1.25 ev after mild annealing.[2] The value found for the process which causes a decrease in conductivity on annealing (1) is about 1.2 ev,[2] and for ion conduction itself is 1.06 ev.[2] These values are all quite similar and in view of the history effects with attendant uncertainty in the activation energies for annealing and for changes in conductivity, it may be that all three processes involve the migration of Ta ions as the rate-determining step. Support for this idea is found in the fact that annealing proceeds more rapidly if an electric field is present in the material.

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[2] These energies are for specimens annealed 5 min at 100°C, so that the corrosion rate would be 18.2 Å/sec.

A Study of Cathode Potentials in Aqueous Tungstate Solutions

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ABSTRACT

Cathode potential measurements were used as a means of obtaining information about the cathode process that results in the electrodeposition of tungsten alloys. A special cell designed to apply the Luggin-Haber backside capillary technique was used for making potential measurements during electrolysis. Changes in the observed cathode potential values resulting from varying the cathode current density and the electrolysis solution were recorded. A hypothesis to explain some of the peculiarities of the cathodic reduction of aqueous tungstate solutions is offered.

Pure tungsten has not been electrodeposited in weighable amounts from aqueous tungstate solutions; however, it is known that tungsten readily codeposits with certain other metals, notably Fe, Ni, and Co. Most of the literature reports on W electrodeposition have been concerned with the development of various types of alloy plating baths and the properties of the alloy deposits obtained. There has been very little experimental work reported directed primarily at finding an explanation for the cathodic behavior of tungstate ion in the presence of metal cations, although a catalytic reduction theory

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has been proposed (1) and the mechanism of the tungsten alloys plating process has been studied (2). Solov'eva and Vagramyan (3) measured the potential of deposition of Fe-W alloys and suggested that their results did not agree with the catalytic reduction theory. Hoar and Bucklow (4) compared hydrogen overpotentials on cathodes of Co, W, and Co-W, while Pecherskaya and Stender (5) compared cathodes of Fe and Ni-W. The purpose of the work reported here was to use cathode potential measurements as a means of explaining why it is possible to electrodeposit W alloys but not pure W from aqueous tungstate solutions.

Fink and Jones reported (6, 7) an aqueous carbonate-tungstate plating bath for the electrodeposition of W. Later, it was shown in this laboratory (8) that no metallic cathode deposit was obtained from a carbonate-tungstate type of bath which had been carefully purified to remove traces of Fe. It was also found that a purified carbonate-tungstate bath gave a W-Fe alloy deposit when it was electrolyzed after the addition of small amounts of iron(III) chloride. It was also reported (9) that Fe must be added to the plating solution as simple Fe(III) or Fe(II) cations and that hexacyanoferrate(III) and hexacyanoferrate(II) ions were not effective.

There are numerous published reports of the electrodeposition of W-Fe, W-Ni, and W-Co alloys from various types of plating solutions, but much of the recent work has made use of an ammoniacal citrate type of bath. Since the ammoniacal citrate bath was to be used in this work, a preliminary survey of bath operation was made with the Hull cell (10). It was found, as expected, that Fe, Co and Ni codeposit with W to give alloy deposits on the cathode, and that Cd, Cu, Mn, Ag, and Zn do not codeposit with W from this type of bath at the conditions used. It seemed reasonable to assume that a study of cathode potentials in ammoniacal citrate solutions could lead to an explanation of why W codeposits from these solutions with certain metals but not with others.

Experimental Techniques

The cathode potentials reported in this work were obtained by the direct method using a saturated calomel electrode and the backside capillary reference electrode technique (11-13). This method produces a minimum of distortion of current density distribution by the reference electrode and salt bridge because there is no obstruction between the cathode and the anode of the electrolysis cell. The current density is a little higher around the edge of the hole in the cathode than it is on the surface of the cathode; however, this effect is small if the area of the hole in the cathode is small in comparison to the surface area of the cathode.

The test cell shown in Fig. 1, and called here the cathode potential cell, was machined from a block of Lucite 16.5 cm long, 7.6 cm wide, and 15.2 cm high which was made by glueing together 2.54 cm thick Lucite sheets. The cathode compartment drilled in the block was about 6.4 cm in diameter and 14 cm deep and was centered about 7 cm from one end of the block. The side of this compartment

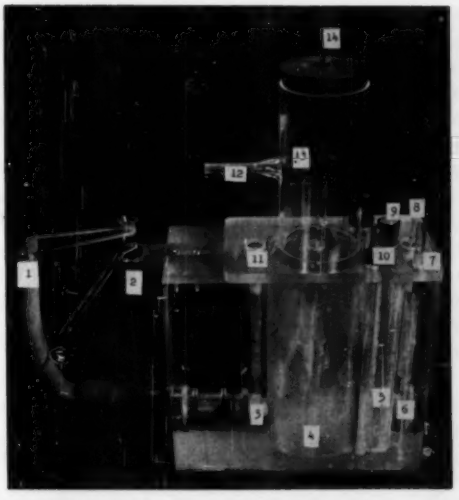

Fig. 1. Cathode potential cell. 1, lead from reference electrode through tubing; 2, side arm extension of calomel electrode; 3, cathode plug, with Pt cathode, fitted into cathode compartment wall; 4, cathode compartment; 5, anode compartment; 6, anode plug, with Pt anode, fitted into anode compartment wall; 7, gas inlet; 8, Pt wire to anode; 9, opening for solution samples; 10, one of two holders for removing diaphragm which separates anode and cathode compartments; 11, Pt wire to cathode; 12, to aspirator; 13, vapor trap; 14, stirrer.

nearest the end was opened and expanded to form the smaller rectangular anode compartment having the same depth as the cathode compartment. A removable Vinyon diaphragm was used to separate the compartments. Both the cathode and the anode were made of Pt and were imbedded in Lucite with the use of a Buehler specimen mounting mold to form electrode plugs which fit into horizontal borings opening into each compartment about 1 cm from the bottom. Each electrode plug was held firmly in position by a stainless steel cover which was fastened to the end surface of the cell by machine screws. This arrangement made it possible to remove the electrodes for inspection and cleaning. Electrical connection to each electrode was made with a Pt wire which rose vertically through the Lucite block and was spring loaded to provide rigid contact with the electrode. A Beckman saturated calomel electrode was used as the combined reference electrode and salt bridge. This electrode approached the cathode from the rear, passed through a 0.3 cm diameter hole in the cathode, and was flush with the surface of the cathode. The effective cathode surface area was 1.20 cm^2. Rubber gaskets and "O" rings provided watertight seals around the reference electrode and the working electrodes. Provision was made for gassing and stirring the solution.

There are two distinctly different electrical circuits in operation when cathode potentials are measured by the method reported here. One circuit consists of the cathode, the anode, and the source of direct current, while the other is made up of the cathode, the calomel reference electrode, and the potential measuring instrument. Practically no current flows in the latter circuit. A 12 v lead storage battery with a suitable control panel supplied

direct current to the cell and a L&N Model 7664, line operated pH (millivolt) meter was used to measure cathode potentials. The control panel was placed between the battery and the cell and consisted of six, linear taper, wirewound, continuously variable rheostats in series, and one in shunt. This allowed the potential applied to the working electrodes to be adjusted from zero to 12 v. A Simpson, Model 373, milliammeter was connected in series in the control panel to indicate the cell current. Although cathode potentials slowly and continuously increased with time with any given voltage applied to the cell they eventually become constant. The time between the application of a given power setting and the leveling off of the cathode potential varied from about 2 hr at very low current densities to about 2 min at high current densities. The signal from the pH (millivolt) meter was fed into a Speedomax recorder. The steady-state cathode potential, as indicated by a vertical trace on the recorder, is the value recorded in the data. The temperature of the cell was maintained at 30° ± 0.5°C by immersing the cell to approximately three quarters of its height in a water bath. The several pieces of apparatus were grounded to a common terminal on a cold water pipe.

Helium was used to sweep oxygen out of the cathode potential cell during each run. It was found that the rate of gas flow, within wide limits, had no effect on the cathode potential or the cell current. The same rate of flow, about two bubbles per second, was used in every run. Since the elimination of convection effects in moderately concentrated solutions being electrolyzed at current densities of from 1 to 15 amp/dm^2 is not possible, the solutions were stirred vigorously during all experiments. Stirring does not eliminate diffusion and migration effects, but it does make them unimportant as compared to convection effects, and therefore the electrolysis proceeds under convection controlled current (14). A glass stirring rod, placed midway between the cathode and anode, was rotated at 1440 rpm. The cathode potential and cell current were not visibly affected by wide variations in stirring speed. The bath pH of 9.6 ± 0.1 was maintained throughout every run by controlled gassing of the cell with anhydrous ammonia vapor.

Twenty-four different types of solutions (Table I) were used for cathode potential measurements. Hereafter, these various solutions are referred to by the symbol indicated under "Bath designation" in Table I. One liter of each of these solutions, except the "W" solution, was prepared from reagent or C.P. chemicals. Two liters of the "W" solution were prepared and one liter of this solution, called "Impure W", was used in making cathode potential runs without further treatment. The second liter of "W" solution was electrolyzed at 10 amp/dm^2 for 30 min between large Pt electrodes to remove, by electrodeposition, traces of other metals. This solution is called "Pure W". Each solution was adjusted to pH 9.6 with NH_4OH before an electrolysis run. Two hundred ml of each solution was placed in the cell for each cathode potential run.

In every solution (Table I) which contains metal ions, the total concentration of all nonalkali metal ions, regardless of species, was 0.3 m/l. Every solution, except the "W" and "NH_3 blanks," contained 0.75 m/l of citrate ion. The high concentration of citrate ions was used to provide an excess above that required for the formation of any possible complexes with metal ions. Furthermore, the large quantity of ammonium hydroxide and ammonium ion were sufficient to form all possible ammine complexes with metal ions and still have available free ammonia. No precipitation of iron(III) hydroxide was observed in the "Fe baths" except on prolonged standing.

Concentration control of the solutions was partially maintained with the use of a Lucite cover over the cell. In no case was more than 50 mg (usually much less) of metal plated on the cathode. Since each fresh 200 ml aliquot used in a run contain approximately 10 g or more of metal, the decrease in metal ion concentration of a solution, due to electrodeposition, was less than 1%. Evaporation losses were too small to be apparent to the eye and such losses were approximately the same in every solution; therefore, increase in concentration due to evaporation introduced only a small and consistent error.

Other experiments had indicated that the use of Fe(III) or Fe(II) as the codepositing metal in the electrodeposition of W alloys made little difference

Table I. Composition of the solutions used in making cathode potential measurements; concentrated NH_4OH was added to every solution to pH 9.6

Bath designation	Bath components	Formula wt	Conc, m/l	Wt, g/l
"W"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$Na_2WO_4 \cdot 2H_2O$	330	0.300	99.0
"Ni"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$NiSO_4 \cdot 6H_2O$	263	0.300	78.9
"W-Ni"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$Na_2WO_4 \cdot 2H_2O$	330	0.150	49.5
	$NiSO_4 \cdot 6H_2O$	263	0.150	39.4
"Cu"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$CuSO_4 \cdot 5H_2O$	250	0.300	74.9
"W-Cu"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$Na_2WO_4 \cdot 2H_2O$	330	0.150	49.5
	$CuSO_4 \cdot 5H_2O$	250	0.150	37.5
"Citrate blank"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
"Fe (III)"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$Fe_2(SO_4)_3$ca.$6H_2O$	ca.508	0.150	76.2
"W-Fe (III)"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$Na_2WO_4 \cdot 2H_2O$	330	0.150	49.5
	$Fe_2(SO_4)_3$ca.$6H_2O$	ca.508	0.075	38.1
"Fe (II)"	$(NH_4)HC_6H_5O_7$	226	0.750	170
	$FeSO_4 \cdot 7H_2O$	278	0.300	83.4
"W-Rich Fe (III)"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$Na_2WO_4 \cdot 2H_2O$	330	0.010	3.30
	$Fe_2(SO_4)_3$ca.$6H_2O$	ca.508	0.145	73.7
"Rich W-Fe (III)"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$Na_2WO_4 \cdot 2H_2O$	330	0.290	95.7
	$Fe_2(SO_4)_3$ca.$6H_2O$	ca.508	0.005	2.54
"Mo"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$Na_2MoO_4 \cdot 2H_2O$	242	0.300	72.6
"Cr"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$Na_2CrO_4 \cdot 4H_2O$	234	0.300	70.2
"W-blank"	$Na_2WO_4 \cdot 2H_2O$	330	0.300	99.0
"NH_3 blank"	A few drops of conc. NH_4OH added to H_2O to pH 9.6			
"Cd"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$CdSO_4 \cdot 8/3H_2O$	257	0.300	76.9
"W-Cd"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$Na_2WO_4 \cdot 2H_2O$	330	0.150	49.5
	$CdSO_4 \cdot 8/3H_2O$	257	0.150	38.5
"Ag"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	Ag_2SO_4	312	0.150	46.8
"W-Ag"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$Na_2WO_4 \cdot 2H_2O$	330	0.150	49.5
	Ag_2SO_4	312	0.075	23.4
"Zn"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$ZnSO_4 \cdot 7H_2O$	288	0.300	86.3
"W-Zn"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$Na_2WO_4 \cdot 2H_2O$	330	0.150	49.5
	$ZnSO_4 \cdot 7H_2O$	288	0.150	43.1
"Mn"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$MnSO_4 \cdot H_2O$	169	0.300	50.7
"W-Mn"	$(NH_4)_2HC_6H_5O_7$	226	0.750	170
	$Na_2WO_4 \cdot 2H_2O$	330	0.150	49.5
	$MnSO_4 \cdot H_2O$	169	0.150	25.4

in the appearance or nature of the deposit. As can be seen in the graphical presentation of the data, there is little difference in the cathode potentials in Fe(III) and Fe(II) solutions in the higher current density (plating) ranges. Although Mo and Cr do not codeposit with W, the cathode potentials in their solutions were observed so that they could be compared with the W solution.

The Pt cathode was prepared for each run by soaking it overnight in concentrated HCl to dissolve the electrodeposit from the Pt and provide a fairly uniform surface. In those cases where Cu or Ag was deposited on the cathode, it was first placed in dilute HNO_3 to dissolve the plate and then rinsed and treated as above. The cathode was polished gently on fine metallographic paper only when absolutely necessary. Before placing it in the cell, the cathode was thoroughly rinsed, brushed with a moderately stiff bristle brush which had been dipped in concentrated HCl, and again rinsed with water. The anode was treated in a similar manner. In spite of these preparations the starting condition of the cathode surface was not exactly the same at the beginning of every run; this is no doubt one of the reasons for the lack of reproducibility of cathode potentials at low current densities.

No difficulty was encountered with the maintenance of the calomel reference electrode. It was allowed to stand between experiments in a saturated solution of KCl. The electrode was checked before each run to be certain it and the side arm extension were full of solution, and to be sure that there was undissolved KCl in the column. No contamination of this electrode by the highly colored electrolysis solutions was observed.

Experimental Results

The solutions used (Table I) are conveniently divided into four classes, according to the type of cathode reaction, as follows: Class 1, solutions from which an alloy deposit containing W was obtained upon electrolysis, i.e., the "W-Ni", "W-Fe(III)", "W-Rich Fe(III)", and "Rich W-Fe(III)"; Class 2, solutions from which a deposit containing no W was obtained upon electrolysis, i.e., the "Cu", "W-Cu", "Zn", "W-Zn", "Fe(II)", "Fe(III)", "Cd", "W-Cd", "Ag", "W-Ag", and "Ni" baths; Class 3, solutions from which no deposit was obtained on electrolysis, i.e., the "Impure W", "Pure W", "Mn", "W-Mn", "Mo", and "Cr" baths; and Class 4, blank solutions, i.e., the "W blank", "NH_3 blank", and "Citrate blank" baths.

The cathode potential data obtained in the various solutions are presented in Fig. 2-5. In Fig. 4 parts of the curves for the "W-Mn" and "Cr" baths and all of the curve for the "Mo" bath are not shown because they lie within a region crowded with curves from other baths and the missing parts of the curves follow the trends shown in the crowded part of the graph. Cathode potentials for values of the cell current below 0.10 ma were not reproducible and are not shown. The potential data are for average values of the cathode potentials for multiple runs with a given solution at any given current. The values of "I" are for the total cell currents of

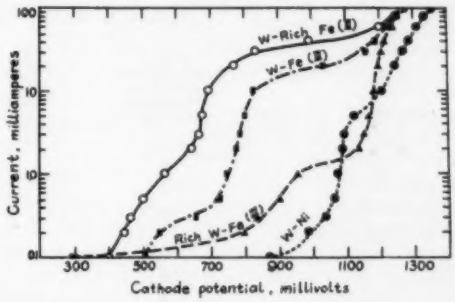

Fig. 2. Class 1 solutions (see Table I for all compositions) give alloy deposits containing W.

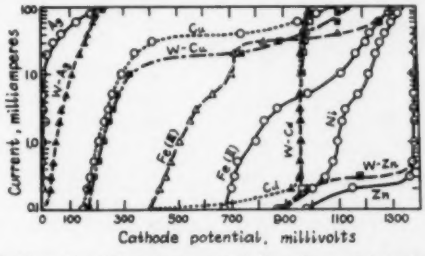

Fig. 3. Class 2 solutions give metal deposits containing no W

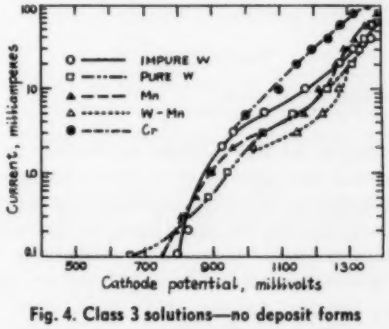

Fig. 4. Class 3 solutions—no deposit forms

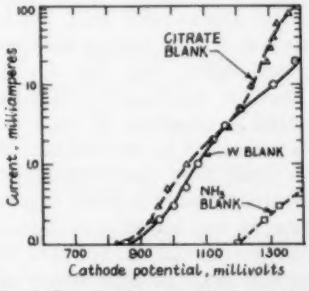

Fig. 5. Class 4 solutions—blank solutions

the electrolysis cell and may be converted to current density in amp/dm² by dividing any value of "I" by twelve.

Shown in Table II are the average maximum deviations of the cathode potentials from the average cathode potential (average of the several runs for a given current density and solution) for each of the 24 types of baths. The greatest deviations of the cathode potential from the average for each type of bath are also shown. The data for this table were compiled from the experimental data tables which are not included here. The average of average maximum deviations is 11 mv, and the average of the greatest deviations is 27 mv. Therefore, the average

Table II. Table of maximum deviations of cathode potentials

Bath designation	Class	Avg of maximum deviations from avg cathode potential	Greatest deviation from avg cathode potential
"W-Ni"	1	9	18
"W-Fe(III)"	1	12	26
"W-Rich Fe(III)"	1	19	26
"Rich W-Fe(III)"	1	12	49
"Cu"	2	14	297*
"W-Cu"	2	14	59
"Zn"	2	5	19
"W-Zn"	2	2	8
"Fe(II)"	2	16	37
"Fe(III)"	2	14	22
"Cd"	2	8	125*
"W-Cd"	2	5	8
"Ag"	2	6	23
"W-Ag"	2	8	16
"Ni"	2	11	36
"Impure W"	3	22	44
"Pure W"	3	27	55
"Mn"	3	10	24
"W-Mn"	3	13	29
"Mo"	3	7	16
"Cr"	3	12	28
"W Blank"	4	6	26
"NH_3 blank"	4	6	8
"Citrate blank"	4	3	8
		11	Avg. 27

* Not included in calculation.

reproducibility of the cathode potentials in all the solutions will be referred to as plus or minus 20 mv from the cathode potential indicated at any particular current density for any given solution. In averaging the greatest maximum deviations of the cathode potentials, two values, 297 mv for the "Cu" bath and 125 mv for the "Cd" bath were deleted before computation. The 297 mv deviation for the "Cu" bath is not due to poor data, but is a cathode potential taken at a very nearly horizontal portion of the "Cu" bath curve (*see* Fig. 3). A horizontal portion of such a curve, i.e., rapidly changing cathode potential at constant "I", is a region where no reaction is occurring at the cathode. In measurements of this type, it is rarely possible to get reproducible results on a flat portion of a curve, and a large deviation is not considered poor reproducibility. The 125 mv deviation for the "Cd" bath is not explained and must be considered experimental error. In general, reproducibility of cathode potentials is better in the intermediate current range, from 0.5 ma to 50 ma, than at very low or high currents probably because there is no reversible electrode reaction to stabilize the cathode potential at very low currents and there are fast irreversible electrode reactions that cause severe oscillation of the cathode potential at high currents. Storage of some solutions for several weeks between the first and duplicate runs also probably affected reproducibility of the results. Certainly with the various baths containing Fe, the relative amounts of Fe(III) and Fe(II) would change on prolonged standing. The Vinyon diaphragm allowed comparatively free passage of the solution, and it, plus the gassing with He, minimized contamination of the cathode by anodic oxygen but could not completely eliminate it. Oxygen arriving at the cathode would, of course, alter the cathode potential. A reaction is occurring at the cathode on rising portions of a log "I" vs. cathode potential curve. The greater the slope, the better is the reproducibility perhaps because a moderately fast series of cathode reactions stabilize the cathode potentials.

It is seen in the curves for the "Cu" and "W-Cu" baths (Fig. 3) that there is a large initial rise in the cell current which indicates a reaction at the cathode, probably the reduction of Cu(II) to Cu(I). This was verified by inspection which showed there was no hydrogen evolution and no deposition occurring for the condition corresponding to the first steep rise of these curves. Similarly, the initial rise in the curves for the several "Fe" baths (Fig. 3) is due to the reduction of Fe(III) to Fe(II).

In Fig. 4 all of the curves are close together. This represents the data for Class 3 solutions, i.e., those baths from which no deposit was obtained upon electrolysis. This figure also shows that the curves for the more active metals are on the right side of the graphs as would be expected. In comparing the curves for the various alloy baths with the baths containing only one metal, it is indicated that, although the presence of the tungstate ion always shifts the codepositing metal ion curve toward the "W" bath curve, the alloy curve is more nearly similar to its pure codepositing metal curve. This influence varies with the relative concentrations of tungsten to codepositing metal as seen with the "W-Rich Fe(III)" and "Rich W-Fe(III)" baths (Fig. 2); nevertheless, the codepositing metal influences the position of the curve more strongly than does the W. It is possible that the shift of the various "W-Fe(III)" bath curves toward the "W" bath curve could be due to a weakly associated complex between Fe(III) and/or (II) ions, tungstate ion, and citrate ion; however, the data do not strongly support the suggestion of such a complex.

The three blank solutions were studied so that their curves could be compared to those for the "W" baths. Fig. 5 shows that the curves for the "W blank" and the "Citrate blank" are similar to the curves for the "Pure W" and "Impure W" baths. This simply indicates that neither tungstate ion nor citrate ion have any special effect on the cathode potential. The curves obtained are due primarily to cathodic hydrogen released from buffered solutions of pH 9.6.

Additional experiments were made with the "Pure W", "W-Cu", "Ni", "Citrate blank", and "Fe(III)" baths to determine when hydrogen evolution began. This was accomplished by careful inspection of the solutions during electrolysis with the aid of a strong light which illuminated the cathode. It was necessary to stop stirring and gassing when making these observations and it was then possible to see the first traces of hydrogen bubble formation. In every case it was observed that hydrogen evolution began at a cathode potential of approximately 900 mv. These data do not support the suggestion that the presence of the tungstate ion in a solution

lowers the overvoltage of hydrogen on the cathode and therefore makes hydrogen evolution easier than tungsten deposition. The lowering of hydrogen overvoltage is not considered a good explanation of why pure tungsten has not been electrodeposited from aqueous solutions.

Latimer (15) gives the following values, in kcal/mole, for the free energy of formation of several aqueous anions: —220 for $WO_4^=$, —218.8 for $MoO_4^=$, —176.1 for $CrO_4^=$ and —107.4 for MnO_4^-. These values indicate very high thermodynamic stability of the aqueous tungstate, molybdate, and chromate ions in comparison to the permanganate ion. It is seen from the data that large energies are necessary to free W, Mo, or Cr from aqueous solutions of their ions and it would be predicted that the electrodeposition of W and Mo from aqueous solutions would be accomplished with difficulty, if at all. It is probable that there is an activation energy barrier, in addition to the free energy of formation, which must be overcome in the reduction of the aqueous tungstate, molybdate, and chromate ions to their respective metals. Cr is electrodeposited only with difficulty and with average cathode current efficiencies of approximately 15%, while pure W and Mo apparently have not been electrodeposited from aqueous solution.

Conclusions

In the plating region, i.e., 24 ma (2 amp/dm^2) and above, the cathode potentials in the various solutions are as follows: "Impure" and "Pure W" baths 1330-1375 mv, "W-Ni" bath 1250-1355 mv, "W-Fe(III)" bath 1100-1275 mv, "W-Rich Fe(III)" bath 780-1265 mv, "Rich W-Fe(III)" bath 1200-1270 mv (Fig. 4 and 2). These data show that the cathode potentials of the four alloy baths come to within 85 mv of the average cathode potential in the "W" baths. Fig. 3 shows that cathode potentials in baths other than those containing Fe or Ni are considerably more than 85 mv from the average cathode potential in the "W" baths. It is emphasized that only comparative values of the cathode potentials shown in these data are considered significant. Similar experiments would show the same relative positions of the cathode potentials of various baths compared with one another as are reported here, but would probably show different absolute values.

The following hypothesis is offered as the explanation of why pure metallic W has not been electrodeposited from aqueous tungstate ion solutions and why W codeposits with certain other metals: (*a*) aqueous tungstate ion has a very high thermodynamic stability which must be overcome to permit deposition of metallic W; (*b*) in the reactions involved in the over-all mechanism of the reduction of the aqueous tungstate ion to metallic W there is probably, in addition to the free energy of formation, an activation energy barrier which must be overcome; and (*c*) the electrostatic repulsion which exists between the negatively charged aqueous tungstate ion and the negatively charged cathode probably prevents the ion from coming sufficiently close to a cathode to allow transfer of the quantity of energy from cathode to ion necessary to overcome the free energy of formation of the ion and the activation energy barrier which probably exists in the reduction process.

Tungsten codeposits with certain metals such as Ni, Co, and Fe from aqueous tungstate ion, metal ion solutions because a freshly deposited surface of the codepositing metal has the catalytic effect of reducing the magnitude of the activation energy barrier which probably exists in the mechanism of reduction of the aqueous tungstate ion to metallic W. In order for a metal to codeposit with W from aqueous tungstate ion, metal ion solutions it must have the following properties: (*a*) the codepositing metal must electrodeposit from the solution under consideration; (*b*) the codepositing metal must be added to the solution as a simple cation; (*c*) the cathode potential in an aqueous solution of the codepositing metal, both with and without tungstate ion present in the solution, must be within 85 mv of the cathode potential in a similar solution containing tungstate ion but no codepositing metal ion while the solutions are being electrolyzed at a current density of 2 amp/dm^2 or higher; and (*d*) the codepositing metal must have catalytic properties, i. e., it will probably be a transition element.

Acknowledgment

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1958 JOURNAL.

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Investigations on the Structure of the Color Compound in Caustic

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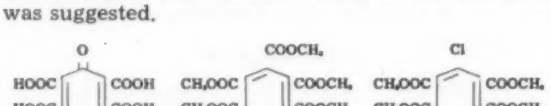
ABSTRACT

The material isolated by Heller from stubs of graphite anodes used in chlorine-caustic soda cells and shown by him to give the color in concentrated caustic soda has been reinvestigated. An extract from the stubs after treatment with nitric acid was found to consist of mellitic acid, pentacarboxychlorobenzene, a tetracarboxychlorobenzene of unknown configuration, and material of unknown structure which is the source of the color. The acids were formed during the treatment with nitric acid. The color forming material seems to be of high molecular weight and structurally more complex than proposed by Heller.

The organic nature of the material giving the familiar color (1) to the evaporated effluent from diaphragm chlorine-caustic soda cells was first established by Heller (2) who proposed for it a pyromellitic acid-chloroquinol structure (I). Since dienones in which a hydrogen is involved are unknown because of their facile rearrangement to the corresponding phenols, a further study of the material was suggested.



I II III

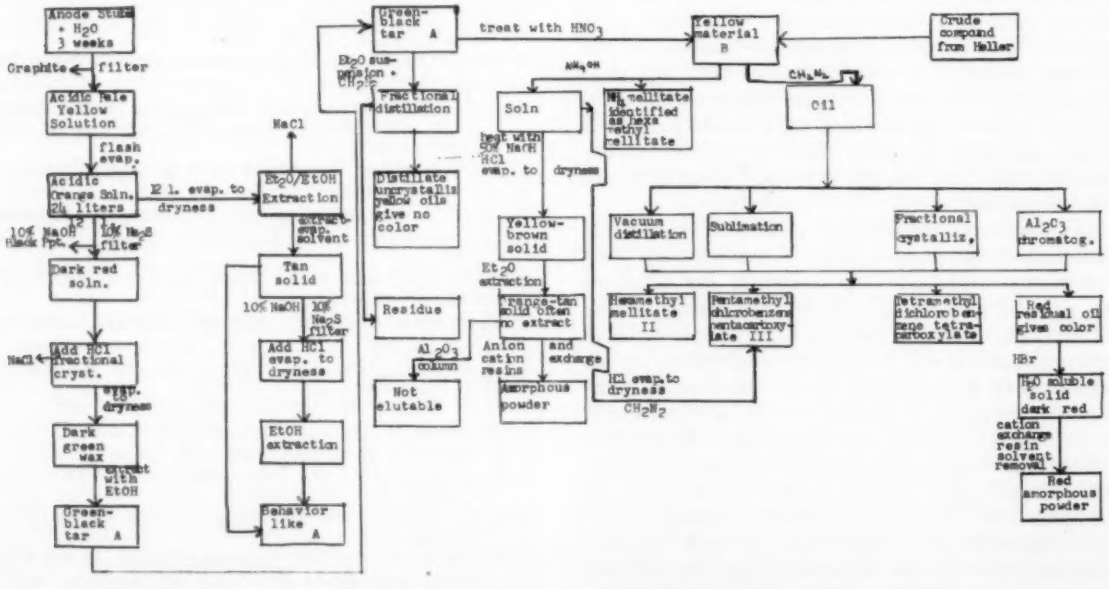
Results

The procedure for the investigation is summarized in the flow sheet (below).

By methylation of the yellow material with diazomethane an oil was obtained from which hexamethyl mellitate (II), pentamethyl chlorobenzenepentacarboxylate (III), and a tetramethyl dichlorobenzenetetracarboxylate were recovered by sublimation, distillation under reduced pressure, fractional crystallization, or chromatographic separation on alumina. The structure of pentamethylchlorobenzenepentacarboxylate (III) was demonstrated by comparison with a sample synthesized from pentamethylchlorobenzene (4). The tetramethyl dichlorobenzenetetracarboxylate was not obtained in sufficient quantities to be characterized. These three compounds did not give a color in 50% caustic.

The red residual oil obtained after removal of these compounds could not be distilled, sublimed, or crystallized and upon treatment with alkali dissolved slowly and gave a reddish purple color. This oil after treatment with HBr gave a solid which was water soluble and gave the reddish purple color with alkali.

An aqueous solution when passed through a cation exchange resin (IR-120H) gave an eluate which, on removal of the solvent, yielded a red amorphous powder. This product could not be purified further by recrystallization and was obtained in insufficient amounts to characterize further.



The mellitic acid could also be isolated from the yellow solid as the ammonium salt hexahydrate by treatment with concentrated ammonium hydroxide. The structure of this salt was demonstrated by acidification and conversion to the methyl ester. The mother liquor from the ammonium mellitate after acidification and methylation gave pentamethyl chlorobenzenepentacarboxylate.

The presence of mellitic acid in the yellow solid raised the question whether this acid was produced from the graphite anodes directly during the formation of the caustic or was formed in the isolation by the recrystallization step using concentrated HNO_3. Following the isolation procedure of Heller but omitting the recrystallization from HNO_3 gave a dark green tar which produced a dark purple color when boiled with 50% caustic. Methylation of an ether suspension of the tar followed by fractional distillation under reduced pressure gave yellow oils which refused to crystallize even when seeded with the esters mentioned. The oils gave no color with 50% alkali. The dark green tar when treated with HNO_3 gave an orange solid which showed similar properties to those of Heller's material. These results indicated that the recrystallization from HNO_3 degraded the more complex compounds formed from the anode during cell operation into the simpler acids. The dark green tar did not contain any suspended carbon so that the latter could be ruled out as the source of the mellitic acid.

This degradation of the complex mixture obtained from the anodes by HNO_3 into simpler compounds suggested a direct study of the compound which formed the purplish-blue color in 50% caustic. The filtrate from the precipitation of the mellitic acid as the ammonium salt was heated with 50% caustic until the bluish-purple color developed. Acidification with HCl followed by evaporation to dryness gave a yellow-brown solid. This material occasionally would give, upon ether extraction in a Soxhlet extractor, a small amount of orange-tan material which produced the bluish-purple color immediately in cold 50% caustic. This behavior was not consistent and, in the majority of the attempts, the extraction did not give any ether soluble solids. Further chromatography was not successful due to the strong adsorption on the column.

Purification of the material by passing through cation and anion exchange resins gave an amorphous powder which resisted crystallization and further purification.

The results obtained with Heller's compound indicated that at least 70% of his material consisted of mellitic acid, pentacarboxychlorobenzene, and tetracarboxydichlorobenzene. The physical data reported for the pyromellitic acid chloroquinol (I) approximate very closely the values for pentacarboxychlorobenzene (IV) as shown below,

	I	IV
%C	39.7	39.7
%H	1.68	1.51
%Cl	11-12	10.66
Neutral equiv.	75	66.5
Mol. wt.	305	337.5

and are in agreement with such a formulation.

The properties of the residue obtained after separating the simpler acids indicate that the compound or compounds responsible for the color in caustic have a higher molecular weight and are more complicated than the compound proposed by Heller.

Experimental[1]

1. *Methylation of Heller's compound.*—An ether solution of 3 g (0.07 mole) of diazomethane was added slowly, with constant swirling, to 2 g (0.006 mole based on mellitic acid) of Heller's material dissolved in 40 ml of methanol or suspended in 40 ml of ether. After the initial liberation of nitrogen, the dark solution was heated at 100° overnight and gave approximately 2.7 g of a dark viscous oil.

2. *Pentamethyl chlorobenzenepentacarboxylate (III) and hexamethyl mellitate (II):*

(*a*) *Chromatography.*—A solution of the oil in benzene was subjected to chromatography on an alumina column followed by elution with benzene and ether. By fractional crystallization of the first benzene eluate 0.6 of crude or 0.15 g of pure III was obtained and from the subsequent eluates 1 g of crude or 0.3 g of pure II.

(*b*) *Sublimation.*—By sublimation under 1 mm Hg pressure in a bath at 135°C there was obtained 1.2 g of crude or 0.65 of pure III. The temperature of the bath was then raised. At approximately 200°C 0.8 g of crude or 0.3 g of pure II sublimed.

(*c*) *Crystallization.*—Fractional crystallization from a mixture of benzene and petroleum ether (bp 60°-70°C) gave 0.6 g of crude II or 0.15 g of pure compound.

(*d*) *Distillation.*—Distillation at reduced pressure (1 mm Hg) gave a fraction boiling between 180° and 200°C which weighed 1 g and contained mostly III. The fraction boiling at 200°-220° gave 0.5 g of crude II or 0.35 g of pure III.

The pure hexamethyl mellitate (II) was obtained from the crude material separated by several recrystallizations from a mixture of benzene and petroleum ether (bp 60°-70°C) and melted at 185°-186.5°C. In some instances decolorizing carbon was used to eliminate traces of red impurities. A mixture with an authentic sample (3) melted at the same point.

The pure pentamethylchlorobenzenepentacarboxylate (III) formed colorless needles after several recrystallizations of the crude ester from a mixture of ether-petroleum ether (bp 60°-70°) and melted at 129°-130°C.

Anal. Calcd. for $C_{16}H_{17}O_{10}Cl$: C, 47.71; H, 3.75; OCH_3, 38.50; mol. wt., 403.

Found: C, 48.12; H, 3.57; OCH_3, 38.70; mol. wt., 418.

This ester was synthesized from pentamethylchlorobenzene (4) in the following manner.

Pentamethylchlorobenzene (2 g) was heated with $KMnO_4$ (30 g) in 500 ml of water containing 5 ml of 10% NaOH at 100° until all the organic material had disappeared. This process required two weeks. The resulting mixture was decolorized with sodium

[1] Melting points and boiling points are not corrected.

bisulfite, acidified, and filtered. The crude acid (1 g) was recovered from the extraction of the filtrate in a liquid-liquid ether extractor as a brown solid. This acid was not purified further but was suspended in 20 ml of methanol and treated with an excess of diazomethane in ether. Recrystallization of the resulting solid several times from a mixture of ether-petroleum ether (bp 60°-70°C) followed by a sublimation at reduced pressure (1 mm Hg) gave long colorless needles (0.25 g) melting at 130°. A mixture with a sample isolated from the caustic color compound melted at the same point.

3. *Tetramethyl dichlorobenzenetetracarboxylate.*—The mother liquors from the recrystallization of pentamethyl chlorobenzenepentacarboxylate were evaporated to dryness and the residue was sublimed at 90°C under reduced pressure (1 mm Hg). The resulting oil after several recrystallizations from a mixture of ether-petroleum ether (bp 60°-70°C) gave small colorless needles melting at 80°-85°C.

Anal. Calcd. for $C_{14}H_{12}O_8Cl_2$: C, 44.34; H, 3.19; OCH_3, 32.74; mol. wt., 379.

Found: C, 44.04; H, 3.28; OCH_3, 32.17; mol. wt., 363, 324.

4. *Ammonium mellitate hexahydrate.*—A solution of 2 g (0.006 mole based on mellitic acid) of Heller's crude caustic color in 10 ml of 95% ethanol containing a few drops of acetic acid, was treated with a small excess of concentrated ammonium hydroxide. The crystals that precipitated on standing were filtered and recrystallized three times from ethanol-water mixtures and gave 0.55 g (16%) of colorless needles that melted with decomposition in the vicinity of 100°C. A sample of caustic color weighing 3.35 g, which had been recrystallized once from 60% HNO_3, gave 1.25 g (22%) of pure ammonium salt. The yield of the ammonium salt ranged from 10-40% depending on the purity of the sample.

Anal. Calcd. for $C_{12}H_{30}O_{18}N_6$: C, 26.09; H, 6.57; N, 15.21.

Found: C, 26.03; H, 6.42; N, 15.31.

By treatment with hot HNO_3 the salt was converted to mellitic acid which melted at 275° with decomposition in an open capillary tube. This acid is reported to melt at 288° in a sealed one (5). A sample of hexamethyl mellitate obtained by reaction of the acid with diazomethane melted at 184.5°-186°C.

The mother liquor after recrystallization of the ammonium mellitate was acidified with dilute HCl and allowed to evaporate to dryness. The tan to brownish-red solids thus obtained were suspended in ether (2 g), and treated with 1.5 g (0.035 mole) of an ether solution of diazomethane at 0°C for 2 hr. The ether was decanted and evaporated. On sublimation at 135°-145°C at 1 mm Hg, the resulting red wax (1 g) obtained gave 0.6 g of a crude product. Recrystallization of the sublimate from an ether-ligroin (bp 60°-70°C) mixture after decolorization with Norit gave colorless needles melting at 129°-130°C. A mixture with a synthetic sample of pentacarbomethoxychlorobenzene showed no depression in melting point.

5. *Isolation of caustic color.*—Used graphite anodes (100 kg) were placed in a wooden barrel containing about 110 l of water and allowed to soak for three weeks. The liquid was filtered from traces of graphite and gave approximately 95 l of an acidic pale yellow solution. This solution was concentrated to 24 l of an orange colored solution using a flash evaporator and was treated in the following two ways:

(*a*) The orange solution (12 l) was made basic with 10% aqueous NaOH and metallic salts were removed by adding a 10% solution of sodium sulfide until precipitation ceased. The resulting mixture was centrifuged from the black precipitate and gave a dark red solution. Acidification with concentrated HCl was followed by repeated fractional crystallization to remove the salt and then evaporation to dryness. The dark green wax obtained was extracted in a Soxhlet extractor with absolute ethanol. Removal of the solvent gave 25 g of a green-black tar which produced a dark purple color when boiled with 50% caustic. Methylation of an ether suspension of this tar with diazomethane followed by distillation at reduced pressure (1 mm Hg) gave only small amounts of a yellow oil which did not crystallize and did not give a color upon heating with alkali. Treatment of the tar with concentrated HNO_3 followed by diazomethane gave hexamethyl mellitate and pentamethyl chlorobenzenepentacarboxylate.

(*b*) The orange solution (12 l) was allowed to evaporate to dryness. By extraction of the resulting dark yellow solid with absolute ether in a Soxhlet apparatus, 9 g of a tan material was recovered. An additional 6 g was obtained by extracting the salts with absolute ethanol. Methylation of these solids with diazomethane, as mentioned above (*a*), with or without the sodium sulfide treatment gave similar oils to those mentioned in (*a*).

Studies on the Isolation of the Caustic Color Compound

Acid hydrolysis.—The residue remaining after removal of the mellitic acid and the chloropentacarboxybenzene as the methyl esters was hydrolyzed with HBr for 10 hr. Evaporation of the solution gave a dark red powder which was separated from inorganic salts by passing an aqueous solution through a cation exchange resin (IR-120H). Removal of the solvent from the eluate gave a red amorphous powder which produced a dark purple color on standing in 50% caustic. This powder gave no ash on prolonged heating and could not be purified further by recrystallization. Aqueous solutions were found to absorb strongly at 2230A and weakly at 2800A in the ultraviolet region. The powder contained chlorine and was obtained in insufficient amounts to characterize further.

Basic hydrolysis.—The aqueous solution remaining from the precipitation of the mellitic acid as the ammonium salt was heated with 50% NaOH until a bluish-purple color developed. Acidification with concentrated HCl followed by evaporation to dryness gave a yellow-brown solid. Extraction of this solid in a Soxhlet extractor with absolute ether

gave a very small amount of orange-tan material which produced the bluish-purple color with cold 50% caustic immediately. The material melted in the vicinity of 170°C with decomposition and gave no color with aqueous ferric chloride.

The compound when added in ether to an alumina column could not be eluted with ether, ethyl acetate, methanol, or water. Treatment of the alumina with alkali followed by acidification gave salts from which the orange-tan material could be again extracted with ether. This material contained chlorine and gave broad absorption bands in the 5.9 μ and 8 μ infrared region. The first band is in the carbonyl region and, due to its broadness, is considered to represent several of these groups. The band at 8 μ is in agreement with such a structure.

The production of the ether soluble compound with alkali was difficult to repeat consistently and prevented the accumulation of enough material to carry out further studies. In most cases ether extraction of the material gave no product.

The yellow-brown material dissolved in water was passed through a cation exchange resin (IR-120H) and then through an anion exchange resin (IR-4B). The red eluate upon removal of the water gave a dark material which turned purple when exposed to light. This purple powder gave absorption peaks in the ultraviolet region at 2245Å and 2230Å and a broad band at 5200Å in the visible region.

Acknowledgment

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Electrolytic Reduction of Nitrobenzene to Hydrazobenzene

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ABSTRACT

In small scale experiments on the electrolytic preparation of hydrazobenzene from nitrobenzene in alkaline emulsion it was found that cathodes of zinc, tin, cadmium, and lead with more than 0.07 mole of spongy layer per square decimeter of the surface were most suitable for the reduction. As base materials for the spongy layers, common metals such as Pb, Fe, and others were found to be useful. At these cathodes, almost quantitative yields of hydrazobenzene were obtained at relatively high current densities with suitable agitation. The mechanism is believed to consist of true electrochemical reduction of nitrobenzene to azoxy- or azobenzene, followed by further chemical reduction of the azobenzene by sponge metal. The mechanism gains support from results of polarographic measurements which show that, while nitrobenzene is an active depolarizer with or without organic solvent in the catholyte, azobenzene is active only when a solvent such as alcohol is present.

In the interest of developing a practical electrochemical preparation of hydrazobenzene, preliminary runs have been made in a larger cell using 1.5 kg of nitrobenzene; material yields of hydrazobenzene up to 90% and current efficiencies of 80% at 17 amp/dm^2 have been obtained, compared with yields of 95% and efficiencies as high as 88% at 30 amp/dm^2 obtained with the small cell.

Interest in the electrolytic preparation of hydrazobenzene originally was based on the commercial importance of this product as an intermediate for acid rearrangement to benzidine. In Japan (1) hydrazobenzene has been produced by reduction of nitrobenzene with finely divided Zn. The cost of this reducing agent makes a practical electrochemical method attractive.

The first electrochemical reduction of nitrobenzene was carried out by Elbs and Kopp (2) at a Ni cathode in aqueous-alcoholic sodium acetate without stirring. The alcohol was added to keep the

Table I. Results of preliminary experiments

Run No.	Catholyte		Cathode	Cathodic current density, amp/dm²	Amount of current, amp-hr	Temp, °C	Yield (%) Hydrazobenzene	Yield (%) Azobenzene	Current efficiency of hydrazobenzene formation (%)
1	$C_6H_5NO_2$:	9.8 g	Fe, smooth	3.0-1.5	11.8	75-78	9	46†	8
	NaOH:	5 g							
	H_2O:	90 cc							
2	H_2O		Ni, gauze	3.0-1.5	10.8	75-78	0	97	0
3	$C_6H_5NO_2$:	9.8 g	Ni, gauze	3.0-1.5	11.1	75-78	53	35	52
	NaOH:	5 g							
	H_2O:	45 cc							
	Alcohol:	45 cc							
4	$C_6H_5NO_2$:	9.8 g	Zn, smooth	3-2	10.9	75-78	84	—	84
	NaOH (5-9%):	100 cc							
5	$C_6H_5NO_2$:	6.2 g	Zn, spongy, on Zn	7.2-4.8	8.5	80-85	92	4.5	72
	NaOH (10%):	60 cc							
6*	$C_6H_5NO_2$:	12.3 g	Zn, spongy, on Zn	12-7.2	16.0	70-80	93	0.6	77
	NaOH (10%):	60 cc							
7	$C_6H_5NO_2$:	12.3 g	Zn, spongy, on Fe gauze	12	17.5	70-80	23	32	17
	NaOH (10%):	60 cc							
8*	$C_6H_5NO_2$:	12.3 g	Pb, spongy, on Pb	12	16.0	70-80	90	3.3	75
	NaOH (10%):	60 cc							

* Toluene added to catholyte when conversion of nitrobenzene to azobenzene was approximately complete.
† Some azoxybenzene included. Runs No. 1-4, area of cathode, 80 cm², unglazed earthenware diaphragm; Runs No. 5-8, area of cathode, 42 cm², asbestos diaphragm.

azoxy compound in solution so that it could be reduced to hydrazo, which could then be oxidized to the azo by any remaining nitrobenzene or nitrosobenzene, according to the scheme of Haber (3). To obtain good current efficiency, Elbs and Kopp found it necessary to reduce the current density to about one fourth of the initial value in the final reduction of azo to hydrazo. McKee and Gerapostolou (4) using concentrated solutions of aromatic sulfonates to keep the depolarizers in solution, reduced nitrobenzene to hydrazobenzene at several cathodes, including Pb, Sn, and Zn, and with the addition of various salts. Their results were complicated by the formation of considerable amounts of aniline in the presence of copper sulfate or at bronze cathodes; they noted solubility of Pb and Zn cathodes in the alkaline electrolyte, as well as the beneficial effect of stirring, in increasing the rate of reduction of azobenzene.

Reduction of the nitro compound to the hydrazo without the use of a blending agent is described chiefly in early patent literature (5). In this work nitrobenzene, suspended by agitation in NaOH electrolyte of concentration up to 5%, was reduced at various cathodes including Fe, Ni, and Pb. Although conditions of electrolysis are inadequately described and identification of products often is insufficient, it was in this work that the importance of agitation as well as the effectiveness of addition of metals such as Zn, Sn, and Pb in promoting reduction beyond the azo level was first recognized. Some of this early work has been cited as showing that control of potential can determine the identity of the product obtained. Other patent literature of somewhat later date (6) describes the reduction of suspended nitrobenzene at about 90°C to hydrazobenzene at current densities up to 0.1 amp/cm² when Pb was added to the electrolyte. The use of hydrocarbons such as benzene as a solvent to keep the cathode surface free of adherent deposits was also introduced in some of this early work.

Most recently Dey, Govindachari, and Rajagopalan (7) reduced nitrobenzene to hydrazobenzene on a 1000 g scale in 10% NaOH at an Fe cathode with PbO added. They noted the deposition of spongy Pb on the cathode, but failed to confirm the effectiveness of some addition agents, including tin and zinc oxides, in promoting the formation of hydrazobenzene.

It was the purpose of the present research to clarify some of the points raised in the early literature, to investigate possible mechanisms whereby the electrolytic reduction of nitrobenzene can be directed to hydrazobenzene, and if possible to devise a practical electrochemical method superior to the usual zinc powder-alkali reduction.

Apparatus and Recovery of Products

The cell used for the preliminary experiments of Tables I and II consisted of a cylindrical glass container, 7 cm in height and 6.5 cm in diameter, centrally located within which was a porous pot diaphragm[1] to isolate the anode. A Ni plate within the porous pot served as anode, and the cathode was a sheet of any desired metal bent into the form of a cylinder approximately 3 cm high and resting against the wall of the cell vessel. In the catholyte space, which held approximately 60-100 cc of electrolyte, was a thermometer and a glass stirrer rotating at 1000-2000 rpm. For all small scale runs except those of Tables I and II an improved cell was used.

It consisted of a cylindrical glass beaker 8 cm in height and 9 cm in diameter on the bottom of which rested a Pt or Ni plate serving as anode. Supported above the anode and centrally located within the cell vessel was a glass cylinder 11 cm in height and 6 cm in diameter. The bottom of this cylinder was

[1] Made of unglazed earthenware or common asbestos cloth in three layers.

Table II. Effect of repeated electrolysis with a smooth and a spongy zinc cathode

Run No.	Catholyte	Cathode	Cathodic current density, amp/dm²	Amount of current, amp-hr	Material yield of hydrazobenzene (%)	Temp, °C	Current efficiency, %
1-a	$C_6H_5NO_2$: 9.8 g. NaOH (5-10%) : 100 cc.	Zn, smooth	2-3	10.9	84	92°-96°	84
1-b	(a)		2-3	12.0	81	92°-96°	73
1-c	(a)		2-3	12.0	86	92°-96°	78
1-d	(a)		2-3	12.0	85	92°-96°	77
2-a	$C_6H_5NO_2$: 12.3 g. NaOH (5%) : 60 cc.	Zn, spongy	12	17.5	77*	70°-80°	60
2-b	(b)		12	15.0	92	70°-80°	82
2-c	(b)		12	16.3	89	70°-80°	73
2-d	(b)		12	15.0	91	70°-80°	81

Run No. 1—Area of cathode 80 cm², unglazed earthenware diaphragm.
Run No. 2—Area of cathode 42 cm², asbestos diaphragm; toluene added.
* A low yield resulted from the inclusion of a part of the product in the diaphragm newly used.
(a) The restored catholyte of the same composition as in 1-a using the catholyte from the former run.
(b) The restored catholyte of the same composition as in 2-a using the catholyte from the former run.

closed with a diaphragm made of one layer of common asbestos cloth, as used for water electrolysis, which was treated with cement to adjust the porosity. Inside the cathode chamber formed by the glass cylinder, a horizontal metal disk 5 cm in diameter was connected to a vertical rod, stirring being accomplished by moving the rod and cathode disk up and down with an amplitude of 3 cm at 100 times/min (100 oscillations/min). The cell was provided with cover with reflux. After a reduction, the cooled catholyte separated into crude hydrazobenzene crystals along with an oily layer and an aqueous solution. The crystals were separated by filtration and dissolved in benzene to remove metallic contaminants. The benzene solution was combined with the oily layer which had been separated from the aqueous solution. After the benzene had been removed under diminished pressure, the solid residue was washed with 2% acetic acid to remove aniline, then with water, dried at 65°C, and weighed. It was then converted into benzidine by treating with 170 cc of 3.5% HCl at 55°-60°C for 4 hr. The undissolved residue, consisting mainly of azobenzene, was dried and weighed. The amount of hydrazobenzene was calculated by difference. The aqueous filtrate was steam distilled to remove aniline and the distillate acidified with acetic acid and combined with the 2% acetic acid wash solution described above. The amount of aniline in the combined distillate and wash was determined as tribromoaniline.

Results and Discussion

Results of preliminary experiments are summarized in Table I. In general, these confirm results of previous investigations reported in the literature. For example, runs 1, 2, and 3 show that with insoluble cathodes such as Fe and Ni, a substantial yield of hydrazobenzene can be obtained only if a solvent is added, as in run 3, to keep the azobenzene in solution. The higher efficiencies possible with Zn as cathode material are confirmed by results of run 4, *et. seq.*, of Table I. Note that the use of soluble Zn, even in the form of a smooth sheet, gives material yield and current efficiency of a higher order than the insoluble Fe and Ni, while the use of spongy Zn or Pb permits an increase of two to fourfold in current density without much sacrifice of current efficiency. The spongy metals were obtained by preliminary electrolysis in NaOH electrolyte, to which metal salt had been added, until the surface of the cathode appeared to be completely covered with electrodeposited sponge. Inferior results obtained with the Zn sponge when deposited on Fe gauze are attributed to incomplete coverage.

Toluene was added to remove coatings of azobenzene and other intermediate products which accumulate on the cathode and interfere with the electrolysis. It was added in runs 6 and 8 at about the time the nitrobenzene had been completely converted to the azo level. In these small scale experiments, the addition of the hydrocarbon did not affect the results very much when the catholyte was thoroughly agitated. However, on a manufacturing scale, it was found that smooth continuous operation seemed to be impossible without the addition of these hydrocarbons.

The results of two series of repeated electrolyses, one with smooth Zn and the other with a spongy Zn electrode are shown in Table II. In these experi-

Table III. Effect of alkali strength on formation of hydrazobenzene from nitrobenzene

Catholyte	Cathodic current density, amp/dm²	Amount of current, amp-hr	Yield (%) Hydrazobenzene	Azobenzene	Aniline
$C_6H_5NO_2$: 9.8 g NaOH (10%) : 100 cc	15	12.0	88	6	0.4
$C_6H_5NO_2$: 9.8 g NaOH (3%) : 100 cc	11	12.3	83	12	1.4

Cathode, spongy Zn on Zn; anode, Pt; anolyte, 100 cc 10% aqueous NaOH; temp, 75°-90°C.

Table IV. Reduction of nitrobenzene at spongy cathodes

Cathode	Cathodic current density, amp/dm²	Amount of current, amp-hr	Yield Hydrazobenzene, g	%	Azobenzene, g	%	Aniline, g	%
Pb	30	18.0	7.0	96	0	0	0.2	3
Cd	30	15.6	7.0	96	0	0	0.3	4
Zn	30	13.5	7.0	96	0	0	0.2	3
Sn	30	12.7	7.1	97	0	0	0.1	1

Anode, Pt; anolyte, 100 cc 10% aqueous NaOH; catholyte, 9.8 g nitrobenzene, 90 cc 10% aqueous NaOH, 10 cc benzene; 5.9 amp; temp, 57°-60°C.

Table V. Efficiency of different cathodes in reduction of nitrobenzene

Cathode	Cathodic current density, amp/dm²	Yield of hydrazobenzene g	Yield of hydrazobenzene %	Current efficiency %
Pb	30	4.7	65	65
Cd	31	4.8	66	66
Zn	29	6.0	82	82
Sn	36	6.4	88	88

Amount of current, 10.9 amp-hr; temp, 75°-80°C; other conditions as in Table IV.

ments the cathode and the catholyte were used in four successive runs. In both series the efficiency was maintained, although at different levels, depending on the cathode. Evidently no substance which would inhibit the reaction had accumulated.

From the preliminary work it was concluded that the electrolytic preparation of hydrazobenzene by reduction of emulsions of nitrobenzene in dilute alkali, without organic solvents, was a practical objective, and that the use of spongy forms of alkali soluble metals as cathode surfaces held promise of high current densities and relatively pure products. Accordingly, with the improved cell described above a more rigorous investigation of critical conditions was undertaken. For the preparation of the spongy cathodes the deposition of 0.07 mole of spongy metal/dm² of cathode surface was adopted as standard. This amount is relatively large compared with the coverage used in other investigations (4, 7), i.e., 0.019 and 0.004 mole/dm². Benzene was added to the catholyte to keep the cathode clean.

Table III compares 3% and 10% NaOH as catholyte under otherwise similar conditions of electrolysis. Since the stronger alkali gave higher yield of hydrazobenzene at considerably higher current density, 10% NaOH was used as catholyte in all subsequent experiments.

Four runs were carried out using Pb, Cd, Zn, and Sn as the cathode surface. The electrodes were prepared by depositing the spongy metal from catholyte initially containing, respectively, 3.0 g PbO, 3.7 g $CdSO_4$; 8/3H_2O, 4.1 g $ZnS_4O \cdot 7H_2O$, and 3.2 g $SnCl_2 \cdot 2H_2O$. Each surface metal, except Sn, was deposited on the same metal in massive form as

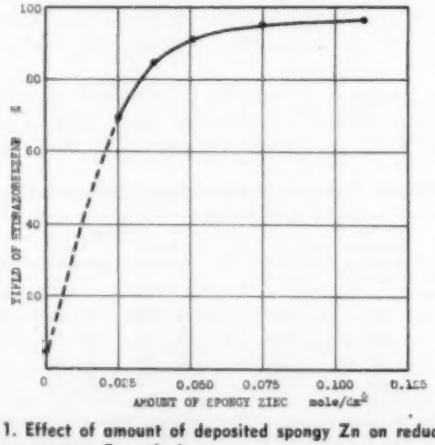

Fig. 1. Effect of amount of deposited spongy Zn on reduction of nitrobenzene at an Fe cathode.

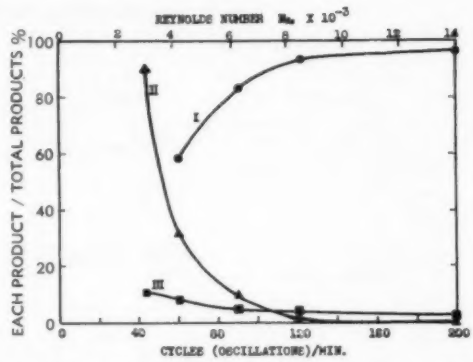

Fig. 2. Effect of agitation on yield of products. Curve I, hydrazobenzene; curve II, azobenzene; curve III, aniline.

base. Spongy Sn was deposited on Pb base. In these runs electrolysis was continued until azobenzene was completely reduced. The completion of the reduction was determined by the disappearance of the red color of azobenzene. Under the conditions of Table IV, it is seen, all four metals were about equally suitable for the formation of hydrazobenzene, giving almost quantitative yields. However, to determine which electrode of the four was the most efficient, electrolyses were carried out using in each case only the theoretical current.

In view of the rate of reduction Zn and Sn showed their superiority over Cd and Pb, Table V, and with them current density could be raised to about 30 amp/dm² without loss of current efficiency.

Since alkali soluble metals were observed to be corroded during the electrolysis, they seemed to be of limited usefulness in practice as base material of cathodes even if a large amount of spongy surface metal were used. Alkali insoluble metals, therefore, should be preferable, but of course would have to be covered thoroughly with surface metal. A high

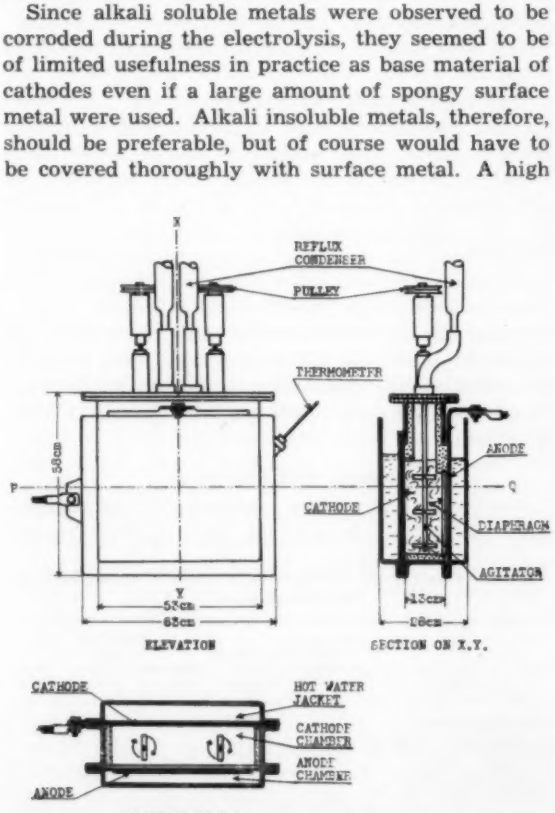

Fig. 3. Details of large scale cell

Table VI. Effect of base metal on reduction at a spongy Zn cathode

Cathode base metal	Cathodic current density, amp/dm²	Amount of current, amp-hr	Yield of hydrazobenzene g	%	Current efficiency, %
Zn	24.5	12.9	7.0	96	82
Pb	24.1	12.5	6.8	93	81
Fe	23.9	12.6	6.9	94	81

Anode, Pt; anolyte, 100 cc 10% aqueous NaOH; catholyte, 9.8 g nitrobenzene, 100 cc 10% aqueous NaOH, 10 cc benzene; temp, 60°-70°C.

overvoltage metal, such as Pb, would appear to be the best choice as the base.

Pb is less active as a surface metal as described above, so when covered with a large amount of preferred surface metal such as Zn, Pb was found to be resistant to corrosion when used as base metal. Fe was similarly useful, provided that it was well covered with active sponge. Table VI shows the results of two cathodes made by depositing the standard amount of Zn sponge on Pb and Fe, a catholyte containing 4.1 g $ZnSO_4 \cdot 7H_2O$ being used in each case for the formation of the sponge, compared with the spongy Zn cathode used in former runs.

It is clear from the table that, with thorough coverage, high conversion and current efficiency can be obtained with any of the two base metals as well as zinc base. However, when Fe, a low overvoltage metal, is used practically as the base, the amount of spongy Zn gave a marked influence upon the yield of hydrazobenzene. Fig. 1 shows that if the amount of Zn sponge is below about 0.05 mole/dm² the yield of hydrazobenzene is greatly decreased. It is believed that the amount of Zn used by Dey, *et al.*, (7) was too small for good results.

Rate of agitation also has been shown to be a critical factor in obtaining high conversion to hydrazobenzene. The oscillation was varied up to a rate of about 200 cpm in a series of experiments, results of which are shown in Fig. 2. Above about 100 oscillations/min uniformly high conversion to hydrazobenzene was obtained, and the amount of azobenzene and aniline[2] in the product fell to a minimum. Below this rate, corresponding to a Reynolds number of about 7000, the yield of hydrazobenzene fell off rapidly, while the proportion of other reduction products rose. The curves of Fig. 2 indicate that the yield of desired hydrazobenzene is influenced by the particle size of the emulsion, and that with any cell design the agitation must be at least sufficient to give particles small enough to produce the desired result.

Preliminary Large Scale Runs

The work with the small experimental cell identified the principal conditions necessary to obtain consistently high conversion of nitrobenzene to hydrazobenzene at high current efficiency and practical current density. A cell capable of using at least 1.5 kg of nitrobenzene per run was constructed and three runs were carried out in it.

The cell is a rectangular sheet iron vessel 63 x 28 x 58 cm high, provided with a rubber-lined iron cover with openings for gas vent, reflux, and two stirrers (diameter, 8 cm) for agitation of the catholyte. The vessel is partitioned as shown in Fig. 3 to provide a hot water jacket and a cell spacing of 15 cm.* Ni plated Fe with an active area 44 cm x 34 cm is used as anode. The cathode, in direct contact with the partition built into the vessel, is a lead sheet covered with spongy Zn with apparent area 48 cm x 31 cm. A sheet diaphragm (48 x 23 cm) near the anode is the product of Nippon Tokushu Togyo Company, Nagoya, Japan. It has a composition of 90% Al_2O_3 and 5%-6% SiO_2, and porosity of 35.6%. Inner surfaces of the cell vessel are lined with cement.

[2] The formation of aniline seems to be due to the incomplete conversion of phenylhydroxylamine to azoxybenzene.
* The distance from the anode to the cathode.

Table VII. Separation of reduction products (Run No. 1)

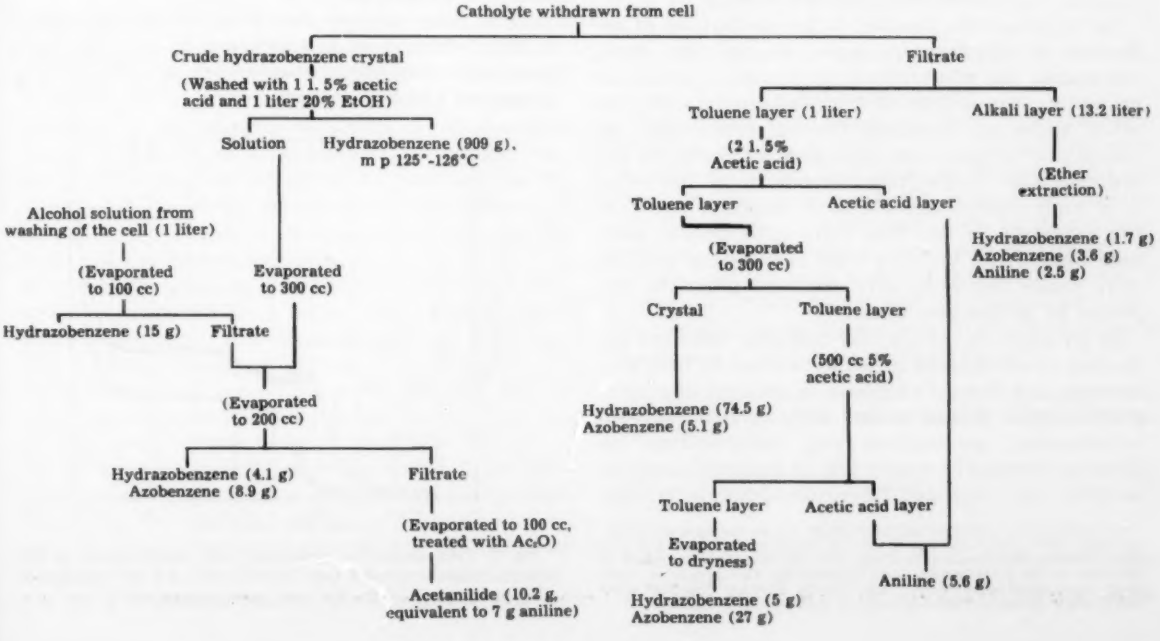

Table VIII. Three large scale experiments

	Run No. 1	Run No. 2	Run No. 3
Catholyte, $C_6H_5NO_2$:	1.5 kg	1.5 kg	1.5 kg
Water:	14 l	13 l	[a]
NaOH:	1.5 kg	1.5 kg	[a]
Toluene:	1.5 l	1.5 l	[a]
Temperature[b]	90°C	90°C	90°C
Amperage:	220-280	235-270	250-280
Mean cathodic current density (amp/dm^2):	16.7	17.2	17.6
Voltage[c]:	8.8-9.8	9.6-10.2	8.6-9.7
Amount of current,			
Ampere hours:	1888	1830	1701
Per cent of theoretical:	116	113	104
Rate of agitation (rpm):	300	300	300
Material yield (%),			
Hydrazobenzene:	90.1	89.5[d,a]	
Azobenzene:	4.0	4.4	
Aniline:	1.3	2.3	
Current efficiency hydrazobenzene (%):	78	83[a]	

[a] Run 3 was a continuation of Run 2. After removal of crude hydrazobenzene by cooling the catholyte from Run 2, 1.5 kg nitrobenzene and sufficient water and toluene to restore the original proportions were added; the restored catholyte was used as starting catholyte for Run 3. Material yields and current efficiency are for combined Runs 2 and 3.

[b] This is about maximum when toluene was used.

[c] Large ohmic drop through the diaphragm. It can be reduced to a suitable value by decreasing the amperage so as to give the maximum economical efficiency.

[d] Of the total yield from Runs 2 and 3, 2004.4 g hydrazobenzene, 902 g was obtained as crude crystal by cooling the catholyte from Run 2; 1030 g was obtained similarly at the end of Run 3, and 72.4 g was obtained by further processing the catholyte in accordance with the scheme of Table VII. 97.7 g azobenzene and 52.6 g aniline were also recovered from the final catholyte.

The procedure for recovery of products from the large cell follows closely that used in the small scale experimental work and is given in Table VII.

Details of the three runs made are given in Table VIII. The cathode was prepared by electrolysis in catholyte initially containing 145 g of Zn dust until 0.11 mole of spongy metal had been deposited per dm^2 of surface of the Pb base. The anolyte in each run was 10 liter of 20% NaOH.

Polarographic Measurements

In the literature, theories of the mechanism of reduction of nitrobenzene have, on the one hand, recognized the effectiveness of organic solvents in promoting conversion to hydrazobenzene. On the other, there has appeared the suggestion that the reaction is voltage-controlled, and is favored by the use of a high overvoltage cathode or of the oxide of a high overvoltage metal as addition agent to the catholyte (7, 9). The early experiments were only qualitative, and if a high overvoltage cathode were really desirable, then mercury might be expected to be the best choice.

In an effort to explain the difficulty with the reduction of azobenzene or azoxybenzene to hydrazobenzene at a Ni or Fe cathode in alkaline emulsion, polarographic measurements were carried out with nitrobenzene, azobenzene, and azoxybenzene, in aqueous alkaline emulsion[5] and in aqueous-alcoholic solution. An improved Heyrovsky-Shikata polarograph made by Yanagimoto Company, Kyoto, Japan, (Type PS, Model 52) was used in connection with a galvanometer having sensitivity of 3.29 x 10^{-8} amp/mm. The sensitivities used were 1.65 x 10^{-8} and 1.65 x 10^{-7} amp/mm. The usual cell, not H type, employing a saturated calomel reference electrode, was used. As cathode, both the usual dropping mercury electrode and a micro rotating metal electrode were used. The t value of the dropping mercury cathode, 30 cm high, was 1.0-1.5 sec. The rotating cathode consisted of a section of wire, 0.2 mm in diameter with available area of 0.03 mm^2, sealed in a glass tube. The stem of the cathode was rotated at 1000 rpm.

[5] Polarograms in alkaline emulsion were not of the true emulsifying state with agitation, but saturated solution of azoxy and azo after allowing the emulsion to stand for 1 hr. Work on the effect of agitation on the polarograms at an emulsifying state was later made using azoxybenzene emulsion. The results showed that the wave height grew linearly with the rate of agitation.

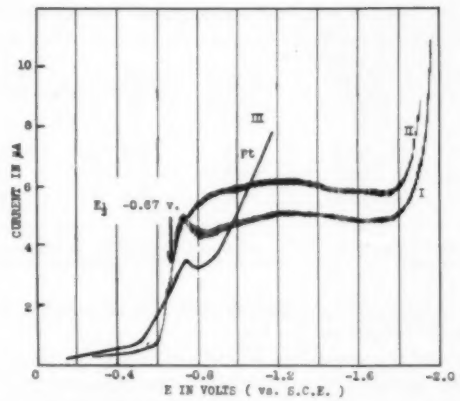

Fig. 4. Polarograms for nitrobenzene. Curve I, 1 x 10^{-3} m/l nitrobenzene in 5% aqueous NaOH at a dropping Hg electrode, 20°C; curve II, 1 x 10^{-3} m/l nitrobenzene in 40% aqueous alcoholic solution (pH 12.1) at dropping Hg electrode, 20°C; curve III, 1 x 10^{-3} m/l nitrobenzene in 5% aqueous NaOH at Pt microcathode, 20°C.

Polarograms for nitrobenzene are shown in Fig. 4. In both aqueous emulsion and in aqueous-alcoholic solution with the Hg cathode, and with both Pt and Hg cathodes in the aqueous emulsion, they show the typical wave with E ½ at about −0.67 v, which is very near the value found by Shikata (10) about thirty years ago.

It is fairly certain that these waves correspond to the reduction of nitrobenzene to nitrosobenzene and phenylhydroxylamine, which in alkaline medium react to form azoxybenzene.

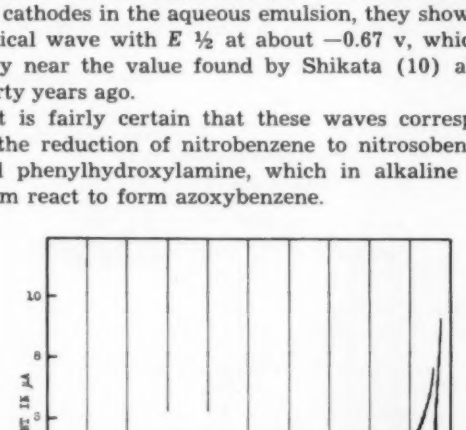

Fig. 5. Polarograms for azobenzene and azoxybenzene in 40% aqueous alcoholic solution (pH 12.1). Curve I, 2 x 10^{-3} m/l azobenzene, 20°C; curve II, 2 x 10^{-3} m/l azoxybenzene, 20°C.

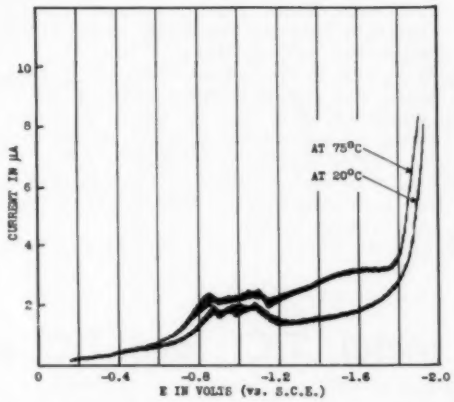

Fig. 6. Polarograms for saturated solution of azoxybenzene in 10% aqueous NaOH at 20° and 75°C.

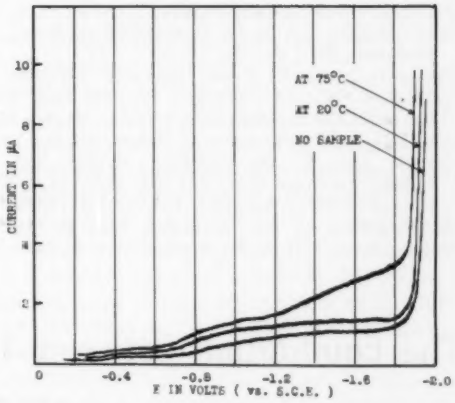

Fig. 7. Polarograms for saturated solution of azobenzene in 10% aqueous NaOH at 20° and 75°C.

Polarograms for azoxy- and azobenzene are shown in Fig. 5-7. In 40% aqueous-alcoholic solution at *p*H 12.1 (in $Na_2B_4O_7$-NaOH buffer), each of these compounds gave one wave of typical shape with $E\frac{1}{2}$ at −0.74 v for the azoxy and −0.88 v for the azo compound. These potentials are appreciably lower than that of hydrogen evolution at a nickel microcathode.

In contrast, the polarograms of the azoxy- and azobenzene in aqueous alkaline emulsion show little evidence of reduction even at elevated temperature. For azoxybenzene the graphs of Fig. 6 show a small wave at about −0.8 v, about the same value as observed for $E\frac{1}{2}$ in aqueous-alcoholic solution. However, the polarograms for azobenzene in Fig. 7 show no distinct wave prior to the hydrogen discharge.

The polarographic study has shown that nitrobenzene can act as a depolarizer in either aqueous emulsion or aqueous-alcoholic solution. However, of the intermediate reduction products between nitro- and hydrazobenzene, azoxybenzene is highly resistant and azobenzene almost completely resistant to further reduction in aqueous emulsion. Since azobenzene is almost completely insoluble in aqueous alkali, and since it becomes an active depolarizer under conditions when its solubility is increased by addition of organic solvent, it is believed that the difficulty in carrying the reduction of nitrobenzene to the hydrazo level is explained, not by any inadequacy of the overvoltage of the cathode, but by the insolubility of the intermediate azobenzene.

If this view is correct, it must follow that the effectiveness of certain metals in promoting formation of hydrazobenzene in the absence of organic solvents is explained on a basis other than electrochemical reaction. It is suggested that the effectiveness of these metals is explained by chemical reduction of the azo compound at the cathode. In this view the reductant would be the metal, and the function of electrode reaction would be to restore the oxidized or ionic form of the metal to the metallic condition for further reduction of azobenzene. The metal thus would function as a hydrogen carrier as already proposed (8) for the reduction of 2-amino-4-chloropyrimidine and its methyl compound to corresponding 2-aminopyrimidines at Cd and Zn cathodes. And it may be that, if cathodes of alkali soluble spongy metal and high current density have been used from the commencement of the reduction of nitrobenzene as in this work, the over-all reductions would mainly be the chemical reaction at the cathode, rather than the electrochemical one.

Conclusions

1. With the help of polarographic measurements it has been shown that the difficult step in the formation of hydrazobenzene from nitrobenzene in alkaline emulsion is reduction of azoxybenzene and, especially azobenzene.
2. The reduction of azoxybenzene and azobenzene is helped by the presence of organic solvents which keeps these compounds in solution.
3. In the absence of an organic solvent, operation with an alkali emulsion of nitrobenzene can give good results if a cathode carrying a suitable amount of a spongy layer of Zn, Sn, Cd, or Pb is used. Under these conditions yields and efficiencies are very high at a relatively high current density. High temperature is preferable and the catholyte must be well stirred.
4. The process is applicable to large scale work.

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The Equilibrium between Titanium Metal, $TiCl_2$, and $TiCl_3$ in NaCl-KCl Melts

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ABSTRACT

The equilibrium between solid titanium metal, di-, and trivalent titanium chlorides dissolved in an NaCl-KCl melt was measured under carefully controlled experimental conditions. Divalent titanium was found to be the predominant valence state in the melt, for temperatures of 700°-800°C. The "apparent" equilibrium constant (mole fractions replacing activities) for the reaction

$$TiCl_3\ (NaCl\text{-}KCl\ melt) + 1/2\ Ti^\circ\ (c) = 3/2\ TiCl_2\ (NaCl\text{-}KCl\ melt)$$

was calculated and found to be a function of the total titanium concentration in the melt. Limited data indicated that the equilibrium is exothermic in agreement with expectation.

Procedures for making pure Ti metal, either on a laboratory or production scale, involve, almost without exception, reduction of titanium halides. In many of these procedures (electrowinning, Kroll process, sodium reduction process) the reduction is accomplished in the presence of a salt melt composed of alkali or alkaline earth chlorides. In the presence of this solution phase, titanium tetrachloride undergoes stepwise reduction to the trivalent, divalent and, finally, zerovalent state depending on the amount and strength of the reducing agent employed. In electrowinning of Ti, the molten salt will contain various proportions of di- and trivalent Ti [tetravalent Ti is only slightly soluble in salt melts (1)] depending on whether it is in the strongly reducing zone near the cathode, or in the oxidizing zone near the anode.

The present state of knowledge of the equilibrium relations between the Ti halides in salt melts is meager; probably the only work known to date is that of Mellgren and Opie (2) on the equilibrium between $TiCl_2$, $TiCl_3$, and Ti° in the presence of an $SrCl_2$-NaCl melt. They measured the equilibrium concentration of $TiCl_2$ and $TiCl_3$ for the reaction:

$$2TiCl_3(melt) + Ti^\circ(C) = 3TiCl_2(melt)$$

as a function of total Ti concentration, the ratio $NaCl/SrCl_2$, and temperature.

The present study is similar to that of Mellgren and Opie except that the salt melt was the equimolar mixture of NaCl and KCl. It is hoped that by studies of this kind the complex chemistry of titanium halide reduction may be better understood and more economically controlled in commercial practice.

Experimental

The desired equilibrium between Ti metal and dissolved titanium chlorides was established by addition of $TiCl_4$ to the NaCl-KCl melt in contact with excess metallic Ti. In this way, $TiCl_2$ and $TiCl_3$ were formed *in situ* by the reaction between $TiCl_4$ and Ti°, with the result that the problem of preparing pure $TiCl_2$ and $TiCl_3$ to use as melt constituents was obviated.

In essence, the method may be described as follows. The NaCl-KCl melt, containing excess solid Ti, was held in a Vycor tube under a purified argon atmosphere. An argon-$TiCl_4$ gas mixture was then bubbled through the melt briefly in order to introduce titanium chlorides to the melt. After each addition of $TiCl_4$, the melt was sampled at successive time intervals. The samples of solidified melt were then analyzed for the content of Ti^{2+}, Ti^{3+}, and Ti^{4+}.

Materials.—Titanium metal, prepared by decomposition of TiI_4, was obtained from the Foote Mineral Co. It was used in the form of rods (0.8 cm diameter, 3.8 cm length).

The salt mixture was made from equimolar amounts of reagent grade NaCl and KCl. Prior to placing the salts in the cell, they were oven dried at 110°C. Further dehydration of the salts was accom-

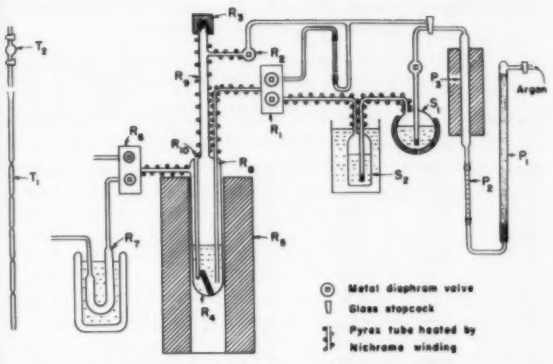

Fig. 1. Simplified schematic diagram of equilibration apparatus

plished by vacuum treatment after they were placed in the cell (*see* below). The $TiCl_4$ was a special purity product (99.99% $TiCl_4$) obtained from the National Bureau of Standards.

Apparatus.—A simplified diagram of the equilibration apparatus is given in Fig. 1; it consists of four principal sections as follows: P, the gas purification train; S, the $TiCl_4$ saturation device; R, the reactor for equilibration of the melt; and T, the sampling device.

With the exception of certain valves noted below, the entire apparatus was constructed of Pyrex and Vycor. Vycor was used for those parts heated above 450°C. Graded seals were used to connect Pyrex and Vycor parts. For those parts of the gas train which were not required to handle $TiCl_4$ vapors, standard vacuum stopcocks and joints, lubricated with silicone grease, were used. No grease was found, however, that would withstand the solvent action of hot $TiCl_4$ vapor. Therefore, in those parts of the apparatus which contain $TiCl_4$, diaphragm-type, high-vacuum valves (Hoke, 411 Series) were used. These valves, which have a Teflon gasket, gave excellent service, and no corrosion of any of the parts was observed. Kovar-to-glass seals were used to connect the Pyrex lines to the diaphragm valves.

To prevent condensation of $TiCl_4$ asbestos-covered Nichrome wire was wound on the glass tubing carrying these vapors. The temperature of the windings was controlled by Variac transformers. For the same reason, valves which must handle $TiCl_4$ vapors must be maintained hot. This was accomplished by enclosing the valves in transite boxes which were heated by Nichrome windings. The valves were operated by extensions of their stems which passed through the face of the heated boxes.

P-Gas purification.—Tank argon was passed through two $Mg(ClO_4)_2$ drying towers, P_1; then through an all-glass, float-type flowmeter, P_2; and finally through a getter consisting of sponge Ti held in a Vycor tube, P_3. The getter was heated by a furnace to 850°C.

S-$TiCl_4$ saturation.—Purified argon was first passed into a presaturator, S_1, containing liquid $TiCl_4$. The $TiCl_4$ was maintained at the approximate temperature desired by a heating mantle. The partly saturated gas stream then passed to the final saturator, S_2, which consisted of a glass chamber partly filled with liquid $TiCl_4$. Fritted-Pyrex disks were used in both saturators to disperse the gas stream. The final saturator was immersed in an oil-bath thermostat, controlled to ±0.1°C.

R-Reactor section.—The Vycor equilibration cell, R_1, was 4.6 cm O.D. and 40 cm in length. A gas inlet tube, R_2, was sealed into the top of the equilibration cell. Either pure A or an A-$TiCl_4$ mixture could be bubbled into the melt through this tube. The diaphragm valves in box R_3 were used to change from pure A to the A-$TiCl_4$ mixture. The cell also contained a Vycor thermocouple well, R_{10}. The melt temperature was determined with a calibrated Pt-Pt 13% Rh thermocouple and a L&N precision thermocouple potentiometer.

Sealed into the top of the cell was a glass sampling-chimney, R_9, 40 cm long and 13 mm O.D. At the top of the chimney was a Teflon tube which had been force-fitted to the Vycor. The top end of the Teflon tube was closed by means of a Teflon cap, carrying a female thread, which screwed to a male thread on the Teflon tube. To ensure a tight seal, a small Teflon cone was fitted into the beveled top of the Teflon tube, and was held tightly in place by the pressure of the screwed-down cap.

Exit gases from the equilibration cell passed through valve box, R_6, and a dry ice-acetone trap, R_7, which collected any unreacted $TiCl_4$. By means of one valve in box R_6, the entire assembly could be connected to a vacuum pump and evacuated to dehydrate the salts.

The equilibration cell, R_1, was heated by a Nichrome-wound furnace, R_8, which had two independent windings. When the current through these windings was properly adjusted the temperature was constant to within ±1°C for a vertical length of 10 cm. The temperature of the melt was controlled to ±1°C by a Brown Electronik Controller, activated by a chromel-alumel thermocouple located close to the main furnace winding.

T-Sampling device.—The sampling pipet, T_1, was made of Vycor tubing, 85 cm long and 8 mm O.D. Constrictions in the pipet were made at intervals of 12 cm to enable small samples to be broken off and analyzed separately. An evacuated bulb, T_2, contained between two stopcocks, fitted to the top of the sample pipet by means of a ground taper joint, and was used to suck up a predetermined amount of melt into the sample tube.

Procedure

Loading of cell and dehydration of salt.—The Ti metal and the oven dried salts were placed in the clean cell before it was sealed to the remainder of the system. The cell was then sealed to the various connecting tubes, and the system evacuated. The cell was heated in intervals of 100°C, to 450°C, with sufficient time allowed at each temperature for the system to be pumped down to 1 μ (Hg) pressure. In this way, the optimum dehydration of the salt was achieved with the least possibility of hydrolysis (3).

When the temperature of the salt reached 450°C, and the system pressure was less than 1 μ (Hg), pure A was admitted to the system through R_5 until the pressure was 1 atm. A steady flow of A at the

rate of 10-15 ml/min was maintained through R_6 throughout the experiment. The temperature was next raised to 700°C and the salt melted.

Admission of $TiCl_4$.—The presaturator, S_1, and the final saturator, S_2, were heated to the desired saturation temperature (110°C). The valves were then switched so that the A-$TiCl_4$ mixture was bubbled through the melt in place of pure A.

Since the rate of A flow and the partial pressure of $TiCl_4$ in the A stream were known,[1] the rate at which $TiCl_4$ entered the cell could be calculated. Since no $TiCl_4$ was detected in the dry ice trap, R_7, in any of these experiments, it could be assumed that it was quantitatively absorbed by the melt. When the desired amount of $TiCl_4$ was added to the melt, the valves were again changed and pure A was allowed to bubble slowly through the melt throughout the equilibration period. Continual flushing with A was necessary to prevent plugging of the tubes with vapor-deposited salts, and also to provide mixing within the melt.

Sampling the melt.—At appropriate time intervals after the introduction of $TiCl_4$ to the melt, a sample was taken for analysis. Valve R_2 was first adjusted so that a rapid flow of A was passing through the chimney, R_6. The Teflon cap on the chimney was then removed, and the sampling pipet slowly inserted into the chimney. The pipet was lowered in slowly so that the A flow would flush the air and desorbed moisture from the pipet. When the tip of the pipet reached the melt level, the evacuated bulb, T_3, was connected to the top of the sampling tube and the lower stopcock of this bulb was opened slowly. The pipet was then withdrawn, the Teflon cap replaced, and the valve R_2 was closed. The pipet was separated from the ground joint by flame-sealing the tube at the top constriction. It was then stored in a dry box to await analysis.

Analysis.—Details of the analytical method are given in (1). Only the sequence of the steps and the broad outline of the methods are given in this paper.

Each sample pipet contained four segments filled with solidified salt. The contents of two or more of the segments were analyzed separately and the average of the results reported as the analysis of the sample. To prepare a sample for analysis the segment was broken inside an argon-filled dry box and the solidified salt (about 3 g) transferred to a special flask. On solidification the melt shrinks away from the walls of the sampling pipet so that a clean and complete transfer of solid salt from each segment was made.

The analytical sequence consisted of three main steps, as follows:

1. The solid salt was reacted with HCl, under an A atmosphere, and the volume of evolved H_2 was measured. The reaction is:

$$Ti^{2+} + H^+ \rightarrow Ti^{3+} + \tfrac{1}{2}H_2(g)$$

This determined the amount of Ti^{2+} in the sample.

2. After oxidation of Ti^{2+} to Ti^{3+}, the total concentration of Ti^{3+} was determined by titration of an aliquot of the acidified solution with standard dichromate solution. The original content of Ti^{3+} in the sample was obtained by subtracting the amount of Ti^{2+} from the total amount of Ti^{3+} in the acidified solution.

3. The total Ti content of an aliquot of the acidified solution was next determined by a volumetric method. The content of Ti^{4+} in the original sample was found by difference between the total Ti content and the sum of the Ti^{2+} and Ti^{3+} contents.

[1] The partial pressure of $TiCl_4$ was calculated from the temperature of the saturator and the vapor pressure data of Arii (4).

Table I. Equilibration of $TiCl_4$ with Ti° in NaCl-KCl (1:1M) melts. Summary of experimental results

Test No.	Equilibration Time, hr†	Equilibration Temp, °C	Melt analysis:* mole/g of melt x 10^4 Total Ti ± 1%	Ti^{2+} ± 1%	Ti^{3+} ± 20%	Ti^{4+} ± 100%
A-1	24	700	3.61	3.14	0.44	0.03
A-2	130	700	3.63	3.25	0.35	0.03
A-3	270	700	3.82	3.45	0.32	0.05
B-1	96	700	5.00	4.36	0.61	0.03
B-2	300	700	5.13	4.68	0.41	0.03
C-1	2	700	4.98	4.36	0.47	0.15
C-2	47	700	5.04	4.54	0.38	0.12
D-1	1	700	8.98	7.94	1.08	0.0
D-2	289	700	9.15	8.34	0.74	0.07
D-3	625	700	9.19	8.37	0.82	0.0
E-1	1/2	700	17.17	14.96	2.11	0.10
E-2	25	700	17.28	15.12	2.08	0.08
E-3	284	700	17.82	15.86	1.84	0.12
F-1	69	780	5.24	4.39	0.85	—
F-2	189	780	5.24	4.62	0.62	—

* Analytical results are the average of two or three samples from one pipet, except for B-2 and F-1, for which only one sample was analyzed.
† Time elapsed after the last addition of $TiCl_4$ to the melt.

Results and Discussion

The results obtained for the equilibration of $TiCl_4$ and Ti°, in the presence of an equimolar mixture of NaCl and KCl, are given in Table I. The data include tests at five different levels of Ti content in the molten salt, two different temperatures, and equilibration times from ½ hr to 625 hr.

The most significant feature of these data is the predominance of divalent Ti in all of the melts. Ti^{2+} constitutes 87-91% of the total Ti dissolved in the molten salt. Most of the remainder of the Ti is present as Ti^{3+}; Ti^{4+} accounts for less than 1% of the total Ti in most cases. These results are in qualitative agreement with those of Mellgren and Opie (2) for the same equilibrium in the presence of a salt melt of NaCl and $SrCl_2$. They found that divalent Ti accounted for 78-93% of the dissolved Ti. They did not report the presence of Ti^{4+}.

Ti^{4+} *content.*—In assessing the significance of the reported values for Ti^{4+}, it should be noted that these were calculated from the difference between two large analytical values, the value for total dissolved Ti less the value for total Ti^{3+} (after oxidation of Ti^{2+} to Ti^{3+}). The average deviation of each of these analytical values, for independent analyses of the same samples, was about 1%. Hence, the results for Ti^{4+} are subject to an uncertainty of 2% of the total Ti content. This uncertainty is in most cases larger than the calculated content of Ti^{4+}. The fact, however, that the calculated content of Ti^{4+} is a positive quantity in 11 cases out of 13 suggests that the samples did contain a small amount of Ti^{4+}.

The authors prefer the explanation that the small content of Ti^{4+} originated from unavoidable oxidation of the sample by air during the analytical procedure, rather than from the equilibrium in the melt. Great care was exercised to minimize sample oxidation during handling and analysis [*see* Reference (1)], but a minor amount of oxidation was probably unavoidable. In support of this hypothesis are the following observations:

1. Analyses of samples in series A and B, (Table I) were made after a modification in analytical procedure designed to further minimize the possibility of sample oxidation. These samples contained the smallest quantity of Ti^{4+}.

2. There is no consistent trend of Ti^{4+} content with total Ti content.

3. $TiCl_4$ is a volatile component in NaCl-KCl melts (1). If there were an appreciable content of $TiCl_4$ in the melt, it should be continually swept out of the melt by the stream of A and be detected in the exit gases. Despite efforts to detect $TiCl_4$ in the exit gas from the apparatus by a variety of methods, in no case was the test positive. Further, there was no reduction in total Ti content of the melt, even after 625 hr. It is concluded that the concentration of Ti^{4+} in equilibrium with Ti° in NaCl-KCl melts is very small, and that the values reported in Table I are undoubtedly too high because of slight oxidation of the samples during handling and analysis. It can be concluded further that reduction of $TiCl_4$ to $TiCl_3$ and/or $TiCl_2$ is very rapid at 700°C, since a ½ hr equilibration period (test E-1, Table I) is sufficient to reduce Ti^{4+} content of the melt to a value below the precision of the analytical method.

Ti^{2+} and Ti^{3+} content.—The analyses for Ti^{2+} on independent samples were reproducible to 1% of the reported values. The values for Ti^{3+}, however, were calculated by difference of two large analytical values, the value for total Ti^{2+} (after oxidation of Ti^{2+} to Ti^{3+}), less the value for Ti^{2+}, each of which is subject to about 1% error. The results for Ti^{3+} are therefore in doubt by ±2% of the total Ti content of the samples. Since values reported for Ti^{3+} amount to only 8-12% of the total Ti content, the uncertainty of the values for Ti^{3+} reported in Table I is about ±20%. This uncertainty should be kept in mind as the significance of the equilibrium data is discussed.

Time of equilibration.—Values reported in Table I show significant changes in concentrations for equilibration times up to 280 hr. The one test carried beyond 280 hr (D-3) failed to show a significant change in concentration when the time of equilibration was extended to 625 hr. In all cases, increases in equilibration time resulted in small increases in total Ti and Ti^{2+}, and small decreases in Ti^{3+}. These changes are consistent with progress of the reaction,

$$Ti^{3+} + \tfrac{1}{2}Ti^{\circ} = 3/2Ti^{2+}$$

from left to right. Since this is the equilibrium that must obtain in the melt, it can be concluded that true equilibrium conditions were not reached for times much less than 280 hr at 700°C.

Table II. "Equilibrium" concentration of $TiCl_2$ and $TiCl_3$

Test No.	Temp, °C	Total Ti content wt %	Mole fractions* $N_{TiCl_2} \times 10^2$	Mole fractions* $N_{TiCl_3} \times 10^2$	$K_x = \frac{N_{TiCl_2}^{3/2}}{N_{TiCl_3}}$
A-3	700	1.83	2.34	0.217	1.65
B-2	700	2.46	3.20	0.281	2.04
D-3	700	4.40	5.87	0.575	2.47
E-3	700	8.54	11.71	1.36	2.95
F-2	780	2.51	3.17	0.425	1.33

* Based on the constituents $TiCl_2$, $TiCl_3$, NaCl, and KCl. The small content of $TiCl_4$ is neglected.

The unusual length of time required to reach equilibrium may be due to an inherently slow rate of reaction at 700°C. It is possible, however, that slow diffusion of Ti^{3+} to the surface of the Ti metal was rate controlling. The surface area of Ti metal was small (the metal was used in the form of rods), and the amount of agitation was slight (the slow bubbling of A, 10-15 ml/min, was the only source of agitation during the equilibration period).

In the discussion which follows, the composition of the melt at the maximum equilibration time (250-300 hr in most cases) is considered as the equilibrium composition. Proof that a state of equilibrium was reached, by experiments designed to approach the equilibrium from the other direction, could not be obtained with the experimental method employed. Since $TiCl_4$ was the source of $TiCl_2$ and $TiCl_3$ in these experiments, the equilibrium was always approached from the high oxidation state side. It would be necessary to add almost pure $TiCl_2$ to the melt in order to approach the equilibrium from the low oxidation state side.

Equilibrium constant.—Melt compositions at maximum equilibration time (presumed equilibrium condition) are converted to mole fractions and reported in Table II. Also reported in Table II are values for the apparent equilibrium constant, K_x, of the reaction:

$$TiCl_3(\text{NaCl-KCl melt}) + \tfrac{1}{2}Ti^{\circ}(c) = 3/2TiCl_2(\text{NaCl-KCl melt}) \qquad (I)$$

$$K_x = N_{TiCl_2}^{3/2} / N_{TiCl_3}$$

N_i = mole fraction of (i), based on the constituents:

$TiCl_2$, $TiCl_3$, NaCl, KCl

(apparent content of $TiCl_4$ neglected)

Fig. 2 shows the variation of K_x with total Ti concentration. For comparison, Fig. 2 also shows the

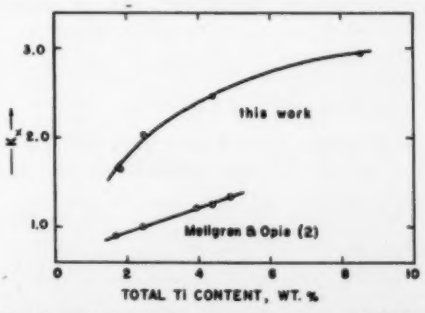

Fig. 2. Variation of K_x with concentration at 700°C

data of Mellgren and Opie (2) who determined K_x for this equilibrium in an NaCl-$SrCl_2$ melt.

The value of K_x does depend on total Ti concentration, both for the results of this investigation and for those of Mellgren and Opie. K_x should be constant if the activity coefficients of $TiCl_2$ and $TiCl_3$ are constant, i.e., if the solutions obey Henry's law over the range of concentrations studied. Since the mole fraction of $TiCl_2$ varies from 0.023 to 0.117 in these experiments, the failure to obey Henry's law is not surprising.

Other interpretations of the equilibrium results were attempted in an effort to explain the trend of K_x with concentration. Mellgren and Opie (2) point out that the assumption that divalent and trivalent Ti are associated into $(TiCl_2)_2$ and $(TiCl_3)_2$ leads to constant K values for the reaction

$$(TiCl_3)_2 + Ti^\circ = (TiCl_2)_3 \qquad (II)$$

This assumption would also lead to relatively constant K values for the results of this investigation. In the absence of more direct proof of association, however, the authors prefer to report K_x for the simpler reaction.

Temkin's rule (5) for the ideal behavior of ionic melts (both in the form of molar ionic-fractions and equivalent ionic-fractions) was applied to the equilibrium results. Values of K for the reactions

$$Ti^{3+} + \tfrac{1}{2}Ti^\circ = 3/2Ti^{2+} \qquad (III)$$

$$TiCl_4^- + \tfrac{1}{2}Ti^\circ = 3/2Ti^{3+} + 4Cl^- \qquad (IV)$$

$$TiCl_6^{2-} + \tfrac{1}{2}Ti^\circ = 3/2Ti^{3+} + 6Cl^- \qquad (V)$$

were calculated in this way. The "constants" so calculated, however, still showed the same trend with concentration displayed by K_x. It must be concluded that insufficient information is available to make a more complete explanation of the equilibrium results.

It is unfortunate that there was time for only one test at a temperature other than 700°C. This one test at 780°C (series F, Table I) did show a significantly larger value for the concentration of Ti^{2+}, and a smaller value of K_x, than test B with the same total Ti content at 700°C. This indicates that reaction (I) is exothermic. The thermodynamic data of Skinner and Ruehrwein (6) and of Sanderson and MacWood (7) show that the reaction

$$TiCl_3(s) + \tfrac{1}{2}Ti^\circ(s) = 3/2TiCl_2(s) \qquad (VI)$$

is also exothermic. Quantitative comparison of ΔH for reactions (I) and (VI) is not possible because the heats of fusion of $TiCl_2$ and $TiCl_3$ are unknown. Mellgren and Opie (2) report no change in K_x with temperature (650°-850°C) for this system, within the accuracy of their analytical method (±5%).

Conclusions

1. The equilibrium of titanium chlorides with titanium metal, in the presence of an NaCl-KCl (1:1M) melt at 700°-780°C is such that divalent Ti is the predominant species (87-91% of the total dissolved Ti).

2. The apparent equilibrium constant, K_x, for the reaction $TiCl_3$(NaCl-KCl melt) + $\tfrac{1}{2}Ti^\circ$(c) = $3/2TiCl_2$(NaCl-KCl melt) has been determined as a function of concentration (1.8-8.5 wt % total dissolved Ti).

3. Based on limited data, the reaction equilibrium was shown to be exothermic.

4. The content of Ti^{4+} in melts equilibrated with Ti metal was proven to be less than 1% of the total dissolved Ti, and is probably much less.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1958 JOURNAL.

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Determination of the Standard Free Energy of Formation of Cuprous Sulfide at 300°C

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ABSTRACT

The free energy change of the displacement reaction

$$2\,Cu(s) + PbS(s) = Cu_2S(s) + Pb(s, l)$$

has been deduced from emf measurements on the cell

$$Cu \mid CuBr \mid Cu_{1.98}S \mid (Cu_{1.98}S, PbS) \mid (PbCl_2 + 1\%\ KCl) \mid Pb$$

between 250° and 350°C. Therefrom a value of −22,607 cal for the standard free energy of formation of Cu_2S at 300°C has been calculated.

To supplement available data, the standard free energy of formation of Cu_xS has been determined with the aid of electrochemical measurements. In order to obtain the free energy of formation of Ag_2S, the cell

$$Ag \mid AgI \mid Ag_2S, S(1), \text{graphite} \qquad (I)$$

has been found to be helpful (1, 2). The analogous cell for Cu_2S cannot be used because Cu_xS reacts with excess sulfur to form CuS and moreover CuI exhibits excessive electronic conduction under oxidizing conditions such as prevail in the presence of liquid sulfur (3-6). To overcome these difficulties, cells involving displacement reactions seem profitable. Since the standard free energy of formation of PbS has been determined recently (2), it seemed expedient to measure the free energy change of the reaction

$$2Cu + PbS = Pb + Cu_2S \qquad [1]$$

In accord with a general survey of the potential use of galvanic cells for such purposes, the cell

$$Cu \mid CuBr \mid Cu_2S, PbS, Pb \qquad (II)$$

may be used under conditions where the three-phase system Pb-PbS-Cu_2S is stable. Preliminary calculations indicated that the standard free energy change of reaction [1] is positive below about 300°C but negative at higher temperatures and, therefore, the three-phase system Pb-PbS-Cu_2S is stable only above about 300°C. At lower temperatures, the three-phase system Cu-Cu_2S-PbS is stable. Thus, the free energy change of reaction [1] in the reverse direction would be obtainable from the cell

$$Pb \mid PbCl_2 \mid PbS, Cu_2S, Cu \qquad (III)$$

Since it seemed desirable to determine directly the temperature at which the standard free energy of reaction [1] changes its sign, an unconventional cell, viz.,

$$Cu \mid CuBr \mid Cu_xS \mid (Cu_xS,\ PbS) \mid (PbCl_2 + 1\%\ KCl) \mid Pb \qquad (IV)$$

was investigated where Cu_xS denotes cuprous sulfide involving a deficit of copper within the homogeneity range of this phase (7). For reasons discussed below, a copper-to-sulfur ratio $x = 1.98$ was used. In view of the finite copper deficit, cuprous sulfide in cell (IV) is not in its standard state.

Cell (IV) may be considered as a double cell involving the individual cells

$$Cu \mid CuBr \mid Cu_xS \mid \text{graphite} \qquad (IVa)$$

and

$$\text{graphite} \mid (Cu_xS, PbS) \mid (PbCl_2 + 1\%\ KCl) \mid Pb \qquad (IVb)$$

where the partial molar free energy of sulfur at the graphite electrodes is determined by the copper-to-sulfur ratio x.

Under conditions involving predominantly ionic conduction in CuBr and $PbCl_2 + 1\%$ KCl, the virtual cell reactions in cells (IVa) and (IVb) on passing two faradays are

$$2Cu + (2/x)\underline{S}\ (\text{in } Cu_xS) = (2/x)Cu_xS \qquad [2]$$

and

$$PbS = Pb + \underline{S}\ (\text{in } Cu_xS) \qquad [3]$$

Thus, the over-all reaction for cell (IV) is

$$PbS + 2Cu + [(2-x)/x]\,\underline{S}\ (\text{in } Cu_xS) = Pb + (2/x)\,\overline{Cu_xS} \qquad [4]$$

and the free energy change ΔF of reaction [4] is

$$\Delta F = -2EF \qquad [5]$$

where E is the emf of cell (IV), and F is the Faraday constant.

Letting

$$\overline{F}_{Cu_xS} = x\,\overline{F}_{Cu} + \overline{F}_S \qquad [6]$$

one obtains for the free energy change of reaction [4] for a given value of x

$$\Delta F = F_{Pb}^\circ + 2\overline{F}_{Cu}(x) + (2/x)\,\overline{F}_S(x) - [(2-x)/x]\,\overline{F}_S(x) - 2F_{Cu}^\circ - F_{PbS}^\circ \qquad [7]$$

and for the standard free energy change ΔF° of reaction [4] as the limiting case for $x = 2$,

$$\Delta F^\circ = F_{Pb}^\circ + 2\overline{F}_{Cu}(x=2) + \overline{F}_S(x=2) - 2F_{Cu}^\circ - F_{PbS}^\circ \qquad [8]$$

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Upon subtracting corresponding sides of Eqs. [7] and [8], it follows that

$$\Delta F - \Delta F^\circ = 2\,[\overline{F}_{Cu}(x) - \overline{F}_{Cu}(x=2)] + [\overline{F}_{S}(x) - \overline{F}_{S}(x=2)] \quad [9]$$

The Gibbs-Duhem equation reads

$$x\,d[\overline{F}_{Cu}(x) - \overline{F}_{Cu}(x=2)] + d[\overline{F}_{S}(x) - \overline{F}_{S}(x=2)] = 0 \quad [10]$$

Substitution of Eq. [10] in Eq. [9] yields

$$\Delta F - \Delta F^\circ = \int_{\overline{F}_{Cu}(x=2)}^{\overline{F}_{Cu}(x)} (2-x)\,d\,[\overline{F}_{Cu}(x) - \overline{F}_{Cu}(x=2)] \quad [11]$$

Under the conditions of the following experiments, the copper deficit δ^* in cuprous sulfide may be represented by (7)

$$\delta^* = 2 - x = 2x_\oplus^\circ \; sinh \{-[\overline{F}_{Cu}(x) - \overline{F}_{Cu}(x=2)]/RT\} \quad [12]$$

where $x_\oplus^\circ$ denotes the ratio of electron holes to sulfur atoms in cuprous sulfide of ideal composition.

Upon substitution of Eq. [12] in Eq. [11], it follows that

$$\Delta F - \Delta F^\circ = -2x_\oplus^\circ\,RT \left\{ \left[1 + \sinh^2 \frac{\overline{F}_{Cu}(x) - \overline{F}_{Cu}(x=2)}{RT} \right]^{1/2} - 1 \right\}$$
$$= -2x_\oplus^\circ\,RT\,\{[1 + (\delta^*/2x_\oplus^\circ)^2]^{1/2} - 1\} \quad [13]$$

whence

$$\Delta F^\circ = \Delta F + \delta^*\,RT \text{ if } \delta^* >> 2x_\oplus^\circ \quad [14]$$

PbS also exhibits deviations from the ideal stoichiometric ratio. An estimate using the most recent data of Bloem and Kröger (8) indicates that under the conditions of the present experiments the contribution to the free energy of reaction [4] due to the nonstoichiometry of PbS is negligible.

Experimental

Predominantly ionic conduction in CuBr at moderately oxidizing conditions has been ascertained with the help of polarization measurements (6). A similar technique has been used in order to investigate $PbCl_2$ and $PbBr_2$, pure and doped with alkali halide.

It is known that $PbBr_2$ and $PbCl_2$ are predominantly anion conductors (9) presumably via anion vacancies (10) when the conductivity is measured under reducing conditions. This is also true for samples doped with alkali halide (11) whereby the concentration of anion vacancies and thus the ionic conductivity is increased.

The total conductivity was determined with the aid of a conventional a-c method. In addition, the magnitude of electronic conductivity has been estimated by determining current-potential curves for cells of type

$$Pb \mid PbCl_2 \mid graphite \quad (V)$$

On applying a voltage below the decomposition potential of $PbCl_2$ with the positive pole on the right-hand side, both chlorine ions and electrons migrate initially toward the graphite electrode. Since chlorine ions are not discharged at the graphite electrode, the chlorine-to-lead ratio at this electrode is slightly increased. Finally, under steady-state conditions, migration of Cl^- ions due to the electrical field is balanced by diffusion due to the concentration gradient, and the current is carried exclusively by electrons moving either as excess electrons or via electron holes.

One batch of $PbBr_2$ was prepared by synthesis from the elements and a second batch was prepared by passing the decomposition products of NH_4Br in a stream of argon over molten commercial $PbBr_2$. Both preparations gave essentially the same results. $PbCl_2$ was prepared by passing the decomposition products of NH_4Cl in a stream of argon over molten commercial $PbCl_2$.

The total electrical conductivity of undoped $PbCl_2$ at 300°C was found to be $1.2 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ which is of the same order of magnitude as that reported by Seith (12). The total conductivity at 300°C of $PbCl_2 + 1\%$ KCl was found to be $1.2 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$, and that of $PbBr_2 + 1\%$ KBr, $1.5 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$.

Plots of the logarithm of the electronic current measured with cell (V) vs. the applied voltage gave essentially straight lines (*see* Fig. 1). This behavior is similar to that reported for cuprous halides (6), but is not amenable to a theoretical analysis because the experimental slopes in Fig. 1 are about four times smaller than suggested by theory.

Since the electronic conductivity in $PbCl_2 + 1\%$ KCl was found to be lower than that in $PbBr_2 + 1\%$ KBr, the former electrolyte was chosen for the following measurements. For a voltage of 0.2 v corresponding to the conditions of the following experiments, the ratio of the electronic current to the total current prevailing between reversible electrodes is found to be 10^{-4} for $PbCl_2 + 1\%$ KCl. Thus predominantly ionic conduction has been ensured.

Cu_2S and CuBr were prepared by synthesis from the elements as described elsewhere (6, 7) and the PbS was a commercial material with a listed purity of 99.67%. The sulfides and the CuBr were pressed into cylindrical pellets, 6.35 mm in diameter by 1-4 mm thick, in a die under about 4000 psi. The copper pellet was 99.999% pure and the lead pellet was of silver-free lead 99.89% pure.

In order to obtain meaningful results, the value of x in Cu_xS must be constant throughout the two Cu_xS pellets in cell (IV). To ensure this condition, the half-cell

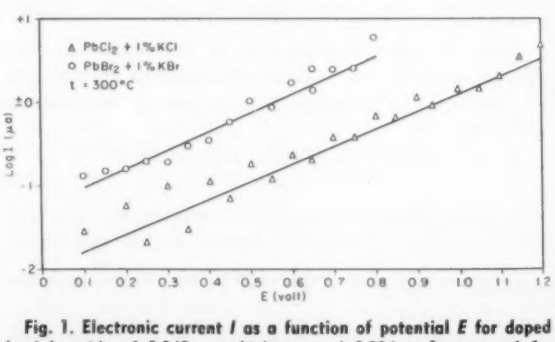

Fig. 1. Electronic current *I* as a function of potential *E* for doped lead bromide of 0.242 cm thickness and 0.316 cm² area and for doped lead chloride of 0.326 cm thickness and 0.316 cm² area.

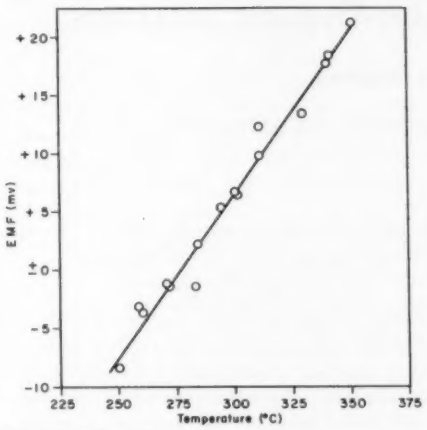

Fig. 2. Emf E of the cell $Cu|CuBr|Cu_{1.96}S|(Cu_{1.96}S, PbS)|(PbCl_2 + 1\%\ KCl)|Pb$ as a function of temperature.

$$Cu \mid CuBr \mid Cu_xS \mid (Cu_xS, PbS) \mid graphite \qquad (VI)$$

was assembled and placed inside a Pyrex vessel as described by Kiukkola and Wagner (2). A positive potential of 0.2 v was applied to the graphite electrode and the cell was then heated to 300°C for 8 hr under an atmosphere of argon to fix the copper-to-sulfur ratio. The potential of 0.2 v was chosen in view of the following compromise. The higher the potential, the lower is the rate of change of the partial molar free energy of copper in the sample with x and, therefore, the more stable is the state "Cu_xS" against perturbations (7). On the other hand, the lower the potential, the lower is the fraction of electronic conduction in both CuBr and $PbCl_2 + 1\%$ KCl.

At the end of the "conditioning process" the connection with the potentiometer was interrupted, cell (VI) was cooled, and cell (IV) was assembled. The doped $PbCl_2$ was pressed into the form of a crucible (2), 10 mm in diameter by 8 mm high, in order to contain molten lead above 323°C.

Cell (IV) was then heated between 250° and 350°C under an atmosphere of argon and the emf was measured.

Fig. 2 shows a plot of a typical run. The results of the measurements on cell (IV) in the temperature range of 250° and 350°C may be expressed by the following equation

$$E(\text{volt}) = (6.5 \pm 1) \times 10^{-4} + 0.3 \times 10^{-6}\,(t - 300) \qquad [15]$$

Discussion

From Eq. [15], the free energy change ΔF of reaction [4] is found to be equal to -300 ± 46 cal at 300°C.

The copper deficit in Cu_2S subjected to an oxidizing potential of 0.2 volt (7) is $\delta^* = 0.02$. Thus it follows from Eq. [14] that

$$\Delta F^\circ = -277 \pm 46 \text{ cal} \qquad [16]$$

Moreover, in view of the temperature dependence of the emf of cell (IV) according to Eq. [15], it follows that $\Delta F^\circ = 0$ at $279° \pm 4°$C. Thus the three phase system $Cu\text{-}Cu_2S\text{-}PbS$ is stable below $279° \pm 4°$C, whereas the three-phase system $Pb\text{-}PbS\text{-}Cu_2S$ is stable above $279° \pm 4°$C.

The standard free energy of formation of lead sulfide has been deduced recently from emf measurements (2),

$$Pb + S = PbS;\ \Delta F^\circ(573°K) = -22{,}330 \text{ cal} \qquad [17]$$

Upon combining Eqs. [16] and [17], the standard free energy of formation of cuprous sulfide is obtained as

$$2Cu + S = Cu_2S;\ \Delta F^\circ(573°K) = -22{,}607 \text{ cal} \qquad [18]$$

On the other hand, one may extrapolate data for the H_2S/H_2 ratio over Cu and Cu_2S determined by Brooks (13) between 342° and 1037°C and by Richardson and Antill (14) between 527° and 1152°C which yield

$$2Cu + H_2S = Cu_2S + H_2;\ \Delta F^\circ(573°K) = -12{,}620 \text{ cal} \qquad [19]$$

Combining the latter value with the standard free energy of formation of H_2S,

$$H_2 + S = H_2S;\ \Delta F^\circ(573°K) = -10{,}039 \text{ cal} \qquad [20]$$

calculated from standard heats of formation and entropy values at 298°K (15) and from enthalpy and entropy increments between 298° and 573°K (16), one obtains

$$2Cu + S = Cu_2S;\ \Delta F^\circ(573°K) = -22{,}659 \text{ cal} \qquad [21]$$

which is in practical agreement with the value obtained in Eq. [18]. This shows the consistency of the various values involved.

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Zinc Standard Potential in Water-Organic Mixtures

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ABSTRACT

The measurement of cell potentials provides one method for testing the predictions of the Debye-Hückel theoretical equations for activity coefficients of electrolytes. The emf of cells: Zn-Hg; $ZnCl_2$(m) (*S*) (*Y*) AgCl(*S*); Ag are investigated to verify the effect of varying dielectric constant in solutions of a 2-1 electrolyte, $ZnCl_2$. (*S*) represents percentages by weight of MeOH, EtOH, and 1,4-Dioxane with water (*Y*). The simple Hitchcock procedure is used to obtain standard cell potentials by graphical extrapolation. Confirmation of theoretical predictions is illustrated by the data obtained. The value for the standard electrode potential of zinc in water is evaluated by direct measurement and confirmed by cell emf data with mixed solvents.

Measurement of reversible cell potentials provides one experimental procedure to test the predictions of the Debye-Hückel equations for activity coefficients of strong electrolytes. Temperature, concentration, ionic charges, and dielectric constant are experimentally controllable factors which affect the values of the coefficients. Whereas considerable data are available for 1-1 electrolytes in mixed solvents (1-3), that for 2-1 and other class electrolytes is much more limited. Moreover, there is some doubt concerning the best value of the standard electrode potential for Zn in water. Harned and Owen (4) accept the value reported by Robinson and Stokes (5) at 0.7634 Int. Volt. Although this is at least 2 mv higher than the average of three previously recorded results at 0.7612 Int. Volt.

The present paper is concerned with evidence which supports the lower value for the Zn standard electrode potential. EMF measurements of cells with mixed solvents demonstrate that only the simplest extrapolation procedure is necessary to obtain standard cell potentials. Further, it may be shown that these are linear with the reciprocal of the dielectric constant of the solvent as given by the Debye-Hückel theoretical equations. Activity coefficients calculated from observed emf data are in good agreement with those calculated from the Debye-Hückel equations.

The standard electrode potential of Zn at 25°C has been determined with cells of the type:

Zn-Hg(2-phase); Zn^{++} X^-(m), MX(s); M

Ag-AgCl (6), Pb-$PbSO_4$ (7), and calomel electrodes (8) have been used as reference electrodes. If the value reported by Robinson and Stokes is omitted, the average of the remaining three results for the zinc standard potential at 25° is 0.7612 Int. Volt. None of the three results deviated from this average by more than ±0.2 mv.

Robinson and Stokes used an extrapolation procedure suggested by Bates (9) which requires the use of the Debye-Hückel extended equation for activity coefficient. They utilized two separate ion size parameters at 3.8 and 5.0A for $ZnCl_2$ in order to extend the linearity of their extrapolation plots through a wide range of salt concentrations.

The same cell type has been used in the present work:

Zn-Hg(2-phase); $ZnCl_2$(m), (*S*), (Y), AgCl(s); Ag

where *S* is the percent by weight of organic solvent, *Y*, that of water, and m is the molality of $ZnCl_2$ in the mixed solvents. MeOH, EtOH, and 1,4-Dioxane were the organic solvents employed in the mixtures so that a range of dielectric constants from 51.9 to 78.4 was available, and conc. to 0.1*M* $ZnCl_2$.

The simple Hitchcock (10) procedure was employed to obtain the standard cell potentials. Particular emphasis was put on measurements with the more dilute solutions so that linear plots could be drawn through a sufficient number of points to assure proper extrapolation in the dilute range below 0.01*M*.

Experimental Procedure

An electrolytic cell was constructed by joining three 1 x 4 in. Pyrex tubes with 6 mm tubing in such manner as to give a top "V" view. The middle tube has sealed at the bottom a reservoir of approximately 1 cc. A Pt wire sealed in this reservoir provides communication to the external measuring circuit.

Two-phase Zn amalgams were deposited electrolytically in this cell by using pure Zn stick anodes, and $ZnSO_4$ solutions. About 1 hr at 1 amp was usually required to produce a firm Zn amalgam, when ½ cc purified Hg is used as the cathode. This procedure makes it simple to prepare amalgams prior to each individual experiment. The cell is washed readily with water and experimental solution before an emf measurement with a particular solution mixture. A zero potential difference between the amalgam and Zn or Hg has been found experimentally (11). The reference Ag-AgCl electrodes were mounted on neoprene stoppers so that they could be inserted in sections of the cell not holding the amalgam. The Ag-AgCl electrodes were prepared by a procedure essentially that recommended

by Brown (12). Number 24 Pt wire is sealed into 4 mm soft glass tubing, and Hg added in the tubing for contact with the external circuit. The wire is silver plated at low current density from a 1% solution of twice recrystallized $KAg(CN)_2$. A cell like that described is used for this purpose, thus separating anode and cathode compartments to prevent free cyanide ion contamination in the Ag. After thorough washing, the Ag is anodized in 0.1*N* HCl. The electrodes were then washed in water and NH_4OH, and reanodized, then again washed in dilute NH_4OH and water. A period of aging is required before these electrodes check against each other with a potential difference of less than ±0.05 mv.

A concentrated $ZnCl_2$ solution was prepared by dissolving a Khabaum grade Zn of 99.966% Zn in redistilled constant boiling HCl solution. With excess Zn present, the final solution had a pH value of near 6.0, but further acid was added to reduce the pH value to 4.4 to prevent hydrolysis in the very dilute solutions.

Methyl and ethyl alcohols were purified in the usual manner, but no attempt was made to collect and store absolute alcohol. Instead, the alcohols were diluted with water, and the alcohol content obtained from density measurements. The 1,4-Dioxane was obtained from Carbide and Chemicals Corp. The liquid was partially frozen, and the melted solid diluted to about 80% Dioxane, and distilled from bright Cu turnings. A constant boiling mixture of known composition is obtained in this way (13), and the distillation could be carried out prior to preparing experimental solutions in order to minimize peroxide contamination.

Each experimental solution was prepared by weighing the concentrated $ZnCl_2$ solution on the analytical balance. Water was added by weight, and the amount of organic solvent to be added could then be calculated to give the desired percent by weight.

Concentrated $ZnCl_2$ was analyzed after preparation by precipitation and weighing of zinc ammonium phosphate and silver chloride. The molality calculated from duplicate set of determinations usually checked to better than 0.0007*M* with a total concentration of 1.4*M* or better.

A conventional potentiometer circuit with a type K L&N potentiometer, a galvanometer with a sensitivity of 0.04 μa/mm division, and a standard Eppley cell with certified Bureau of Standards calibration, were used to measure emfs at 25° ±0.02°C. Readings were sensitive to 0.01 mv. A new amalgam was prepared for each run. After the cell was filled wtih the experimental solution, a flow of purified hydrogen was maintained over the amalgam during all emf measurements. A period of 24 hr was required with dilute solutions to obtain steady readings, but less time with more concentrated solutions. Concentration of $ZnCl_2$ less than 0.004*M* gave erratic results. Two Ag-AgCl electrodes in the cell made it possible to obtain duplicate results. Often, but not at all times, two runs or four separate results were obtained. Since a period of more than 4 years was necessary to obtain all the data recorded here, AgCl electrodes were prepared periodically, but always checked against older electrodes available.

Calculation and Tabulation of Results

Measured emf values of the cells are recorded in Int. Volts.

For 2-1 electrolyte:

$$E = E^\circ - \frac{RT}{n\mathbf{F}} \ln 4m^3V^3 \qquad \text{(I)}$$

in which $V\pm$ is the mean activity coefficient, E the measured emf, E° the standard cell potential, and m the molality.

Rearrangement and expansion gives:

$$E = E^\circ - \frac{3R'T}{n\mathbf{F}} \log 4^{1/3} - \frac{3R'T}{n\mathbf{F}} \log m - \frac{3R'T}{n\mathbf{F}} \log V\pm \qquad \text{(II)}$$

To introduce $f\pm$, the activity coefficient given by the Debye-Hückel equations, the expression:

$$\log V\pm = \log f\pm - \log [1 - .001\ v\ Mxy \cdot m] \qquad \text{(III)}$$

is required. Mxy is the average molecular weight of the mixed solvent, and v the number of ions produced by the electrolyte, and,

$$Mxy = \frac{100}{\frac{S}{Mx} + \frac{Y}{My}} \qquad \text{(IV)}$$

where $R' = 2.303R$; $R = 8.3142$ Int. Joules; $\mathbf{F} = 96{,}500$ coulombs.

For extrapolation of measured emf data to infinite dilution, the Hitchcock method (10) was employed. The Debye-Hückel limiting expression with an added linear team,

$$-\log f\pm = 2A(u)^{1/2} - C'u \qquad \text{(V)}$$

is substituted in (II) after first introducing (III) in (II). Expression (V) is now substituted and on rearrangement and expansion one obtains:

$$E^\circ = E - 0.08873 \times 2A(u)^{1/2} + 0.08873\ C'u - 0.08873 \log [1 - 0.003\ Mxy \cdot m] + 0.08873 \log m + 0.01781 \qquad \text{(VI)}$$

The value of A is derived from the Debye-Hückel theoretical expression:

$$A = \frac{1.824 \times 10^6}{(DT)^{3/2}} \qquad \text{(VII)}$$

Calculations are facilitated by letting $E^{\circ\prime}$ equal

$$E + 0.08873\ [\log m - \log (1 - 0.003\ Mxy \cdot m)] + 0.01781 - 0.08873 \times 2A(u)^{1/2} \qquad \text{(VIII)}$$

and,

$$E^{\circ\prime} = E^\circ - 0.08873\ C'u \qquad \text{(IX)}$$

The last expression provides the linear function by which extrapolation to $u = 0$ may be made.

Calculation is further simplified by defining:

$$E^{\circ\prime\prime} = E + 0.08873\ [\log m - \log(1 - 0.003\ Mxy \cdot m)] + 0.01781. \qquad \text{(X)}$$

and

$$E^{\circ\prime} = E^{\circ\prime\prime} - 0.08873 \times 2A(u)^{1/2} \qquad \text{(XI)}$$

The data are tabulated in Tables I through XIII.[1] These also give the dielectric constant, the Debye-Hückel constant A, the average molecular weight of the solvent, Mxy, and the Debye-Hückel constant B, defined by:

$$B = \frac{5.029 \times 10^{8}}{(DT)^{1/2}} \qquad \text{(XII)}$$

The dielectric constants were those reported by Åkerlof (14) or calculated for empirical expressions suggested by him.

The observed activity listed is that obtained from the extrapolated standard cell potential and cell emf values with different m values; the calculated value is that calculated from the equation:

$$-\log f\pm = \frac{2A(u)^{1/2}}{1 + Ba(u)^{1/2}} \qquad \text{(XIII)}$$

Discussion of Results

Data in Tables I through XIII show extrapolated values for E° which are the standard cell potentials. To obtain these values, the recorded $E^{\circ\prime}$ data were plotted against u. Large 24 in. x 30 in. graph paper made it possible to plot individual points with an uncertainty of ±0.05 mv. The linear graphing fitted most of the points in the dilute range with a precision of better than ±0.1 mv. The extrapolated standard potentials were therefore expected to be read off the plots with this precision. Graphical extrapolations are summarized in Fig. 1-4.

Fig. 1 shows the calculated $E^{\circ\prime}$ values taken some ten years apart. The smooth straight line drawn through these two sets of points indicates the excellent reproducibility attained by the electrode systems, and the simple Hitchcock extrapolation in the dilute range.

Fig. 5 depicts the plots of the standard cell potentials obtained with the three different solvent systems, against 1/D. The data for Fig. 5 are summarized in Table XIV. Linearity is retained through the lowest dielectric constant value with a precision of better than ±0.1 mv. Moreover, each separate plot extrapolates through the same single value, that for the standard cell potential with water and identical with the value for this potential obtained by measurement. This experimental evidence, together with the fact that calculated and observed activity coefficients in all solvents show an average deviation of less than ±0.01 units, supports the value of the standard potential for Zn in water at 0.7610 ±0.0002 Int. Volt.

Harned and Owen (4) report values for the standard electrode potential of the Ag-AgCl electrode in water at −0.2224 Int. Volt, and also give values for this potential in most of the solvent mixtures used in this work, so that the value for the electrode potential for Zn in these solvents could be calculated.

[1] These tables have been deposited as Document 5192 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 5, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for a photoprint or for a 35-mm microfilm. Advance payment is required. Make check payable to: Chief, Photoduplication Service, Library of Congress.

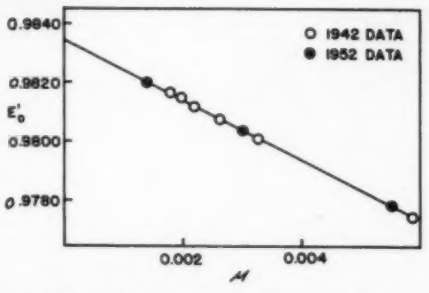

Fig. 1. $E^{\circ\prime}$ values for the cell with water as the solvent, and extrapolation to zero ionic strength.

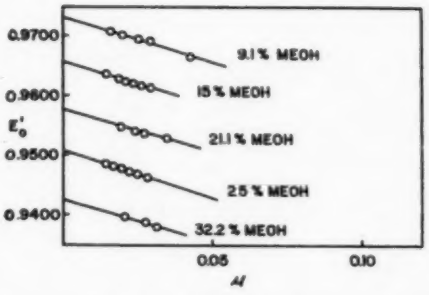

Fig. 2. $E^{\circ\prime}$ values for the cell with MeOH-water solvents, and extrapolation to zero ionic strength.

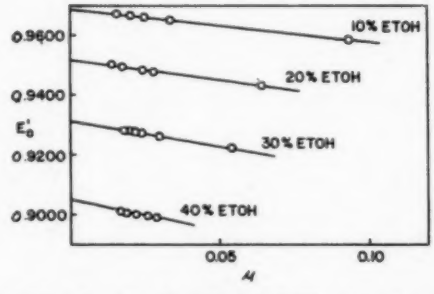

Fig. 3. $E^{\circ\prime}$ values for the cell with EtOH-water mixtures, and extrapolation to zero ionic strength.

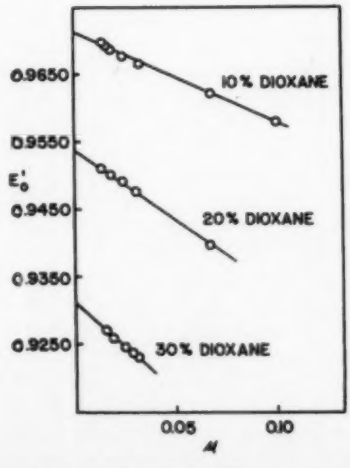

Fig. 4. $E^{\circ\prime}$ for the cell with 1,4-Dioxane-water mixture, and extrapolation to zero ionic strength.

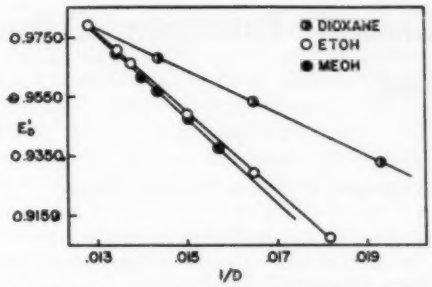

Fig. 5. Standard cell potentials for cells with MeOH, EtOH, 1,4-Dioxane, -water mixtures plotted as a function of $1/D$.

A plot of

$$\frac{2A(u)^{1/2}}{\log f\pm \text{ (obs.)}} \text{ vs } (u)^{1/2}$$

should give a slope of $1 + Ba$. From the data given here, it can be shown that such a plot with all solvent systems results in a value for a of 4.8 ±0.2A and hence justifies the choice of a single ion size chosen in these calculations.

Conclusions and Summary

The cells:

Zn-Hg(2-phase); $ZnCl_2(m)(S)(Y)$, $AgCl(s)$; Ag

have been investigated, with (S) representing mixtures of MeOH, EtOH, and 1,4-Dioxane at different percentages by weight with water, Y per cent. The cell potential with pure water gives a value for $E°$, (Zn/Zn^{++}), 25°C equal to +0.7610 Int. Volt. This is 2.4 mv lower than the result accepted by Harned and Owens, but appears to be adequately supported by the experimental data presented. The activity coefficients from the observed data are in good agreement with those predicted by the Debye-Hückel equations in solvent media of different dielectric constant. The linear variation of the standard cell potential with $1/D$ as given by theory is well confirmed by experimental data, although no simple relationship exists which gives a single linear function with different solvent mixtures of the same dielectric constant.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1958 JOURNAL.

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Preparation of Pure Fused Lithium Chloride-Potassium Chloride Eutectic Solvent

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ABSTRACT

Hydrolytic decomposition occurs during the fusion of a eutectic mixture of lithium chloride-potassium chloride containing traces of moisture if the fusion conditions are not controlled. The resultant contamination by hydroxyl ion greatly lowers the utility of this mixture as a fused salt solvent. The effectiveness of various procedures used for preparation of the fused salt solvent was followed by observation of the characteristic polarographic residual current using a platinum microelectrode. A preparative method is described which involves drying the mixture under moderate vacuum, fusion under anhydrous hydrogen chloride, and removal of the hydrogen chloride from the melt.

For the initial work of a long-term general investigation in fused salt electrochemistry, a eutectic mixture of LiCl-KCl was selected as the fused salt solvent. Advantageous characteristics of this solvent are good thermal stability, wide span of electrolytic decomposition potential, absence of strongly acidic or basic properties, high conductivity and fluidity, and commercial availability of its components as the reagent grade salts. Further, the melting point is low enough and its chemical reactivity is such that Pyrex glass can be utilized as a material of construction. The properties of the solvent thus permit, in theory, a study of the electrochemistry of a wide variety of solutes with a minimum of interference from solvent effects and with only moderate experimental difficulty as high temperature work goes.

In practice, the potentiality of these desirable solvent properties, particularly the wide decomposition potential span, is limited by the purity of the fused solvent which can be prepared. The most troublesome aspect of preparing a pure LiCl-KCl eutectic fusion arises from the highly deliquescent property of the LiCl. Unless special precautions are taken, hydrolytic decomposition occurs as the temperature is raised and HCl is lost from the system. Concurrently, the melt becomes contaminated with alkaline products.

Various methods have been proposed and used to prevent hydrolytic decomposition during the preparation of anhydrous chlorides. The heating of hydrated rare earth chlorides with gross amounts of NH_4Cl is one classic method. For the preparation of fused LiCl-KCl mixtures containing potassium hexachloromolybdate, the method of heating the salt mixture to fusion in a stream of dry, inert gas followed by an electrolysis of the melt for removal of oxygen as molybdenum oxides at the cathode and by volatilization of molybdenum oxychlorides has been used (1). Another procedure involves drying the LiCl and the KCl separately by first slowly heating the salts to between 480° and 500°C under high vacuum (10^{-4} to less than 10^{-6} mm Hg), then mixing the dried salts together under a controlled atmosphere in a dry box, and finally fusing the dry mixture under high vacuum (2, 3). The method to be described here involves drying the eutectic mixture under moderate vacuum, fusing the mixture under anhydrous HCl at atmospheric pressure, and then removing the excess HCl from the fused solvent.

Experimental Procedure

The apparatus used in this work includes the following:

Furnace: Cenco-Cooley No. 13627, 115 V, 700 W, Central Scientific Company, Chicago. A separate heating circuit equivalent to 25% of the original furnace heating capacity was installed in the bottom of the furnace cavity. Only this auxiliary circuit was operated by the furnace controller.

Controller: Wheelco Indicating Controller Model 241-P, Barber-Coleman Company, Rockford, Illinois.

Vacuum Pump: Cenco "Pressovac," Central Scientific Company, Chicago.

Chemicals: Tank gases of the Matheson Company,

Joliet, Ill., were used. The argon was passed over hot Cu to remove traces of oxygen. Both argon and HCl were dried over $Mg(ClO_4)_2$. Reagent grade LiCl and KCl were used to prepare the solvent.

Electrodes: A Pt foil in equilibrium with a dilute solution of Pt (II) in the fused salt solvent was used as the reference electrode. This system has been shown to determine a stable, nonpolarizable reference potential and has been described in various modifications (4-6). The microelectrodes used consisted of 26 gauge Pt wire sealed into Corning 0120 glass with about 1 mm of the wire projecting (total electrode area of 1.4 mm^2) or 18 gauge tungsten wire sealed into Pyrex glass with the wire ground flush to the glass (total electrode area of 0.8 mm^2).

Polarograph: The polarograms reported were observed as automatically recorded curves by using an "Electrochemograph," Type E, Leeds and Northrup, Philadelphia.

Fused salt cell: The cell used is described below.

The cell in which the solvent preparation procedure is completed has been found very useful in performing both chemical and electrochemical experiments. As it is a general tool for fused salt research (6), it is described in greater detail than is necessary merely for use as the solvent preparation vessel.

Fig. 1 is an illustration of the various cell components. The cell as shown is only partially assembled and all of the various components shown are not necessarily to be in use at one time. An explanation of the function of these components serves to indicate which combination is needed for a particular purpose. All of the glass parts are Pyrex (Corning 774) except as otherwise noted.

The side arm tube A is the fused salt container. It is 33 cm long by 6 cm OD and indicates the scale of the illustration. In use, the tube contains fused salt to a depth of about 4½ cm and protrudes from the furnace above the level L-L which is 12 cm from the bottom, but in more recent work has been increased to 15 cm. The melt inside tube A can be divided into several portions by the compartments B which are closed at the bottom by medium porosity fritted glass disks. These portions of melt are then in electrolytic contact with one another but cross-contamination of the compartment contents is prevented. A number 13 rubber stopper C serves to close the tube A and to support within the tube A the inert-gas delivery tube D, the thermocouple sheath E, and various electrodes. Those holes in stopper C which are not in use are closed by glass plugs F.

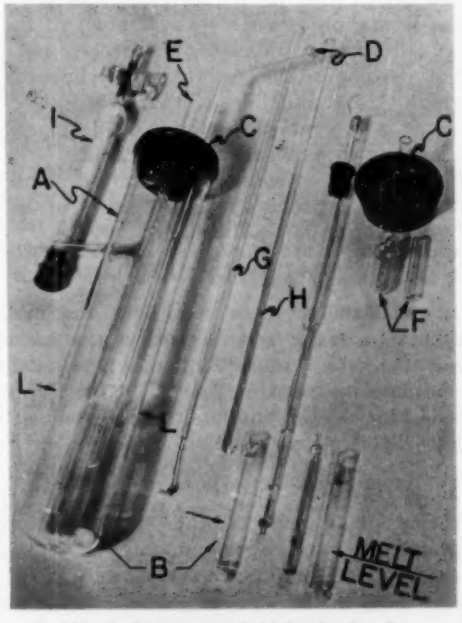

Fig. 1. Components of the fused salt cell

The large holes in stopper C permit easy manipulative access to the interior of tube A. During the experiment, for example, individual compartments can be removed from the system, using hook H, or known amounts of a solute can be added to any one of the compartments within the tube, using platinum spoon G. The entry of air into the system is prevented by an argon atmosphere which blankets the fused salt.

The seven holes in the stopper must have parallel axes and must fit their respective glass parts (10 mm and 16 mm in this case) very snugly but without binding. It has been found advantageous to bore the holes with a drill press, using a regular twist drill. The stopper is first frozen in a dry ice-"Cellosolve" mixture.

A principal advantage of this cell is that several different solution compositions can be maintained at one time in separate compartments in the tube. Thus, a new bath of fused salt solvent need not be prepared for each change of experimental condition. The precise course of an experiment need not be predetermined, since it is a simple matter to alter the composition of a compartment at any time without affecting the composition of the rest of the compartments. This is an extremely valuable advantage in fused salt research.

The fritted barriers of the compartments are very effective for preventing diffusion of a solute out of its compartment. Electrically, the barriers are efficient in that the resistance is but 20 to 50 ohms between two Pt wires immersed in the eutectic solvent of two different compartments.

Preparation of the eutectic solvent is carried out as follows. Reagent grade LiCl and KCl are taken in the proportion 0.59 mole to 0.41 mole and mixed together. The mixture is placed in a suitable vessel and exposed to a vacuum (0.1 to 0.2 mm Hg) for 6 hr to remove excessive moisture so that the material will not cake during the next step. All transfers of the material from this point on must be made as rapidly as possible to avoid excessive pickup of atmospheric moisture. The vacuum-dried mixture is ball-milled to a fine free-flowing powder in a clean, tightly closed jar, using porcelain balls which have previously been leached with 6*N* HCl, rinsed with pure water, and oven-dried. The ground mixture is stored in 1-lb screw-cap jars until needed. It has been kept as long as 1 year without caking, provided that the ground mixture is vacuum-dried

at room temperature for a few hours immediately after being transferred into the 1-lb containers.

A large desiccator having an appropriately drilled Lucite plate serves to sieve the balls from the mixture without undue exposure to atmospheric moisture.

The solvent preparation for an experiment, working from the vacuum-dried, ground mixture, is completed in tube A, referring to Fig. 1. Tube A is fitted with a stopper C carrying a gas delivery tube D and a thermocouple sheath E. All unused holes in the stopper are closed by plugs F. The spherical joint of tube D is connected to a stopcock at which either argon or anhydrous HCl is available at a pressure of 4-5 cm Hg in excess of atmospheric pressure. The sidearm of tube A is fitted with its protective drying tube I, which is in turn connected to a vacuum manifold. With the stopcock of the gas delivery system closed, the system is evacuated to check for the presence of leaks. The system is considered free of leaks if the pressure reading is 0.2 mm Hg or lower. Air is then admitted to atmospheric pressure through the drying tube I.

The charge of ground eutectic mixture is then loaded into the cell through one of the large holes. It should be emphasized that tube A does not contain the compartments B at this point and that the gas delivery tube D is within 1 cm of the bottom of tube A. After loading the charge of eutectic mixture into tube A, the system is maintained evacuated at room temperature for a period of 3 days. The system is next gradually brought to a temperature of 300°C during an 8-hr period by appropriate adjustment of the furnace controls, vacuum being maintained all the while.

Fusion of the charge is effected under the following conditions. Anhydrous HCl is slowly admitted to the evacuated cell through gas delivery tube D until, when the pressure exceeds atmospheric, HCl can be discharged from the cell through the sidearm drying tube I into a disposal sump. A convenient disposal sump for the HCl is the interior of a filter flask which is connected to a running water aspirator, the filter flask being also vented to the atmosphere. A slow flow of HCl is maintained through the salt mixture while the temperature is raised to 500°C, fusion occurring at 352°C.

After fusion, the melt is saturated with HCl which must be removed. Most of the HCl can be removed by evacuating the system for a few minutes with the water aspirator and then using argon to bring the system back to atmospheric pressure. Evacuation of the system with the water aspirator and the refilling with argon is repeated once more.

At this point it is convenient to add the compartments B to the system, if they are to be used in an experiment. Their previous treatment consists of having been thoroughly cleaned, rinsed, and vacuum-dried at 400°C. They are added to the system one by one, while hot, through the large holes in stopper C, using the hook H to make the transfer. The compartments fill by gravity during the final step of the melt preparation.

As a final step, the system is evacuated on the vacuum manifold for 3 hr. The pump is protected from HCl vapors by a 24-in. column filled with an Ascarite-$Mg(ClO_4)_2$ mixture. The system is brought back to atmospheric pressure with argon at the completion of the evacuation period and an inert atmosphere is maintained over the melt for the balance of an experiment by a continuous slow flow of argon. Argon is delivered by tube D to a level just above the surface of the melt.

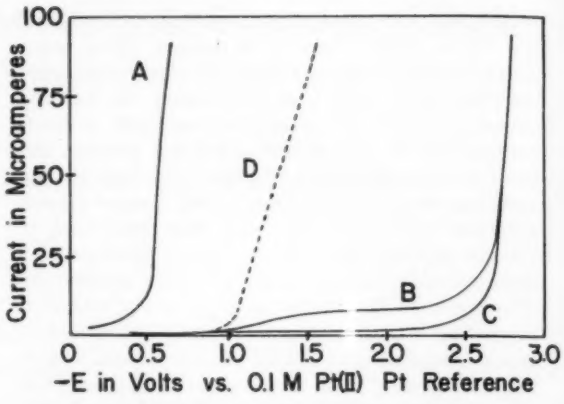

Fig. 2. Polarograms for the eutectic solvent at 450°C. A, solvent still saturated with HCl after fusion; B, after evacuation for 2 hr, most of HCl removed; C, after evacuation for 3 hr, HCl virtually absent; D, typical curve for solvent fused without precaution to prevent hydrolysis.

Results and Discussion

The polarographic method, using solid microcathodes, was found to be an excellent way of detecting the presence of electroactive impurities in the solvent preparations. Curve D of Fig. 2 is a typical polarogram of those observed for the solvents which were prepared by fusion without precaution to prevent hydrolytic decomposition or which were prepared by fusion under moderate vacuum. Evidence of solvent contamination is shown by the rapidly increasing current at −0.9 v. The cathode process giving rise to this current is accompanied by the formation of visible gas bubbles at the microcathode surface, indicating the process not to be solvent decomposition. Another experimental fact suggesting contamination is that the Pyrex container of a solvent so prepared is deeply etched within 1 or 2 hr exposure to the solvent.

The procedure of solvent preparation given here is designed, by provision of an excess of HCl, to shift the hydrolytic equilibrium

$$H_2O + Cl^- \rightleftharpoons OH^- + HCl \uparrow \qquad (I)$$

to the left. Under these conditions the moisture volatilizes from the system without the formation of hydroxyl ion. Alkaline contamination is undesirable because its corrosive attack on the Pyrex cell leads to further contamination of the solvent and because the electrode reaction

$$OH^- + e^- \rightarrow \tfrac{1}{2} H_2 + O^- \qquad (II)$$

interferes with a study of other electrode processes which occur between approximately −1 and −2.5 v vs. the Pt-Pt (II) reference system.

The effectiveness of the preparative procedure given can be judged from curve C of Fig. 2, which

is a polarogram typical of the eutectic solvent prepared as specified. For curve C the residual current preceding the terminal process of lithium metal deposition is less than 3 μa at a microcathode of 0.8 mm^2 area. The inherently wide decomposition potential span of the LiCl-KCl eutectic mixture is thus accessible for the electrochemical study of such solutes as $CrCl_2$, $FeCl_2$, CuCl, $ZnCl_2$, and $MgCl_2$. None of these solutes can be studied at low solute concentrations in the contaminated solvent because reaction (II) is competitive with most of the electrode reactions of interest. Furthermore, the alkaline environment of a contaminated solvent results in precipitation of some of the solutes as insoluble species. The freedom from alkalinity of the solvent when prepared as described is attested by the fact that the above solutes remain in solution and the fact that the Pyrex glassware is only slightly etched after days of contact with the fused salt solvent.

Although reaction (I) is written as an equilibrium, the reaction is not shifted readily to the left once it has proceeded extensively to the right. Fusion of the eutectic mixture without precaution to prevent hydrolytic decomposition yields a solvent the condition of which cannot be made satisfactory by the passage of HCl. The corrective treatment does not serve in place of the preventive treatment.

Data which illustrate the slow release of moisture by the ground eutectic mixture are shown in Table I. These data were obtained by determining the volatile material collected in a trap, cooled with a dry ice-"Cellosolve" mixture, which escaped a 195.4 g sample of the ground eutectic mixture under the conditions indicated. It was concluded that at room temperature and 0.1-0.2 mm Hg pressure the major portion of the moisture is removed from the ground eutectic mixture in 3 days. The numerical values of Gardner, Brown, and Janz (2, 3), reported on an extended study of weight changes as a function of time and temperature of alkali chlorides maintained at 10^{-4} to 10^{-6} mm Hg, cannot be compared to the data of Table I because of the differences in temperature and pressure conditions. Both sets of data yield the same general conclusion, namely, that moisture is tenaciously held by LiCl, even at low pressures.

A summary of observations, based on the results of altering the experimental conditions given above for the preparation of the fused salt solvent, indicates the conditions prescribed to be optimal for the production of a high quality solvent with a minimum of preparative effort for the amounts of solvent required in electrochemical studies.

Table I. Moisture collected from 195.4 g of eutectic mixture

Evacuation* period, hr	Temperature condition	Moisture collected in trap, g	Cumulative moisture collection, g
0-24	Room temp	0.65	0.65
24-60	Room temp	1.00	1.65
60-74	Room temp	0.10	1.75
74-84	Room temp	0.00±0.05	1.75
84-94	Slowly incr. to 245°C	0.15	1.90

* Pressure maintained at 0.1-0.2 mm Hg.

The quality of the solvent preparation, as measured by the polarographic curve, is lowered if the time of the "room temperature" evacuation of the ground eutectic mixture is less than 2 days. During this period the preparative operation requires no operator attention and little in the manner of equipment. Shortening the period is therefore not particularly to be desired. Shortening the period during which the mixture is heated, under vacuum, from room temperature to 300°C is deleterious to the solvent quality. Substitution of the vacuum condition during this step by 1 atm of HCl pressure is also deleterious. Experience shows that the fusion step must be performed under HCl in order to prevent excessive hydrolysis because the vacuum conditions prescribed are insufficient for complete removal of the moisture prior to fusion. Fusion of the mixture at low pressure of HCl is without beneficial effect on the solvent quality. The time required for removal of the HCl from the melt is not appreciably shortened by interrupting the evacuation with frequent flushes of the system with argon.

Several attempts using other means to remove moisture and hydroxyl ion from the melt proved to be unsuccessful. The chemical reaction of either $SOCl_2$ or $SiCl_4$, introduced as the vapor carried by a stream of dry N, constituted the most nearly successful elimination of moisture and hydroxyl ion. The hydrolytic reactions were slow and incomplete under the conditions of the experiments. Use of acidic metal chlorides in the same capacity was ruled out because of the cation contamination thereby introduced into the solvent. Prolonged electrolysis of the melt between graphite electrodes failed to produce a pure solvent, as judged by the polarographic criterion, probably because this method does not eliminate oxide contamination. No noticeable improvement in the residual current characteristic was produced by the scavenging effect of cathodically deposited Li. Melts prepared in contact with Vycor and Alundum containers had the same residual current characteristic as those prepared in Pyrex, indicating the container material to be of little apparent significance.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1958 JOURNAL.

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Technical Note

Crystal Structures of Transition Metal Silicides

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Recently there has been a great interest in the compounds of silicon with the transition metals. Many new compounds have been prepared and their properties studied. In some cases, where the ideal composition was unknown, the phases were given incorrect names, and there has been some confusion as to which phases were meant.

In the following tables an attempt has been made to list the phases which have been reported in each system, their ideal structure type, lattice constants, parameters of one of the type, and adequate references. Compositions given are the ideal compositions, but in many cases actual compositions can deviate widely. For some compounds there are wide homogeneity ranges with varying lattice constants. In this table no attempt has been made to give the range of lattice parameters, for often this is not accurately known. Instead, lattice constants are given for a typical composition. For the case where compounds had been reported with the incorrect ideal composition, a note has been added in square brackets, stating the true ideal composition. All early data which had been given in *kX* units have been converted to Angstroms. The space group notation and positions of the atoms are listed as given in the International Tables (1).

Early work in this field and properties of these compounds have been cited by Schwarzkopf and Kieffer (2), and more recent work by Nowotny and Parthé (3).

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Table I. Structure types of transition metal silicides

Nominal composition	Ti	Zr	V	Nb	Ta	Cr	Mo	W
MSi	Orth.-$TiSi_2$(4)*	Orth.-$ZrSi_2$(7,8)	Hex.-CrSi.(14)	Hex.-CrSi.(14)	Hex.-CrSi.(14)	Hex.-CrSi.(14,38)	Tetr.-CaC$_2$(29)	Tetr.-CaC.(29)
MSi	Structure unknown (5)	Orth.-FeB(7)				Cubic-FeSi (26)		
M_5Si_4		Structure unknown (9); not found by ref.(7); may be part of ZrSi phase region (10).						
M_5Si_3		tetr.-U_3Si_2(11) called Zr_3Si_2 by ref. (9).		[Nb_5Si_3 reported in ref.(21) is $Nb_5Si_{3-x}Cr_xSi_x$ type.		[Cr_5Si_3 reported in ref. (21) and (27) is Cr_5Si_3.	[Mo_5Si_3 reported in ref. (21) is Mo_5Si_3.	[W_5Si_3 reported in ref. (21) is W_5Si_3.
M_3Si_2	Hex.-Mn_5Si_3(6)	Hex.-Mn_5Si_3(12) called Zr_3Si_2 by ref.(9).	[Hex.-Mn_5Si_3 type reported in ref. (15) is ternary compound requiring C or B(16).	[Hex.-Mn_5Si_3 type reported in ref. (12) is ternary compound requiring C or B(16).	[Hex.-Mn_5Si_3 type reported in ref. (24) is ternary compound requiring C, B, or N (16).		[Hex.-Mn_5Si_3 type reported in ref. (30) is ternary compound requiring C (12,16).	
M_5Si_6			Tetr.-Cr_5Si_6(17,18)	Tetr.-Cr_5Si_6(17,18)	Tetr.-Cr_5Si_6(18)	Tetr.-Cr_5Si_6(17,22,28)	Tetr.-Cr_5Si_6(17,22, 28,31)	Tetr.-Cr_5Si_6(17,22, 28,31)
M_3Si_5				Tetr.-Cr_3B_5(22)	Tetr.-Cr_3B_5(22)			
M_3Si_4		Tetr.-$CuAl_2$(11)	[V$_3$Si reported in earlier work does not exist (19).	[αNb_3Si reported in (23) is Cr_3B_4 type. βNb_3Si reported in (23) is Mn_3Si_4 type.	Tetr.-$CuAl_2$(24)	[Cr_3Si reported in ref. (26,27) is undoubtedly Cr_3Si_4		
M_5Si_3			Cubic-"β W"(20)			Cubic - "β W"(26)	Cubic - "β W"(32)	
M$_2$Si-MSi		Probably more than 2 phases near this composition (13). One form is isostructural with $TaSi_{2-x}$(13).		Structure unknown; isostructural with $TaSi_{2-x}$(13). Not found by ref. (9).	Hex.-$Ta_{1-x}Si$ ideal Ni_2Sn type (24). $TaSi_{2-x}$ structure unknown (25). Different from Ta_5Si_3.			

* Another structure has been reported for $TiSi_2$—orthorhombic $ZrSi_2$ form (34).

Table II. Structural data for transition metal silicides (in Angstroms)

$TiSi_2$ — orthorhombic (4) — D_{2h}^{24} — $Fddd$			$Z = 8$			
a = 8.252				8Ti in (a)		
b = 4.782				16Si in (c)	$x = 1/3$	
c = 8.540						
$ZrSi_2$ type — orthorhombic — D_{2h}^{17} — $Cmcm$			$Z = 4$			
$ZrSi_2$ a = 3.721 (8)				4Zr in (c)	$y = 0.109$ (7)	
b = 14.68				$4Si_I$ in (c)	$y = 0.449$	
c = 3.683				$4Si_{II}$ in (c)	$y = 0.750$	
$TiSi_2$ a = 3.62 (34)						
b = 13.76						
c = 3.60$_5$						
$CrSi_2$ type—hexagonal — D_3^1 — $P\,6_122$			$Z = 3$			
$CrSi_2$ a = 4.431 (26)				3Cr in (d)		
c = 6.364				6Si in (j)	$x = 1/6$	
VSi_2 a = 4.571 (14)						
c = 6.371						
$NbSi_2$ a = 4.794 (14)						
c = 6.589						
$TaSi_2$ a = 4.782 (14)						
c = 6.565						
CaC_2 type — tetragonal — D_{4h}^{17} — $I\,4/mmm$			$Z = 2$			
$MoSi_2$ a = 3.206 (29)				2M in (a)		
c = 7.877				4Si in (e)	$z = 0.333$	
WSi_2 a = 3.218						
c = 7.896						
FeB type — orthorhombic — D_{2h}^{16} — $Pnma$			$Z = 4$			
ZiSi a = 6.98$_2$ (7)				4Zr in (c)	$x = 0.17_8$	$z = 0.125_8$
b = 3.78$_6$				4Si in (c)	$x = 0.03_2$	$z = 0.61_1$
c = 5.30$_1$						
FeSi type — cubic — T^1 — $P\,2_13$			$Z = 4$			
CrSi a = 4.629 (26)				4M in (a)	$x_{Fe} = 0.139$	
				4Si in (a)	$x_{Si} = 0.845$	
U_3Si_2 type — tetragonal — D_{4h}^5 — $P4/mbm$			$Z = 2$			
Zr_3Si_2 a = 7.081 (33)				2Zr in (a)		
c = 3.701				4Zr in (h)	$x = 0.17$ (11)	
				4Si in (g)	$x = 0.37$	
Mn_5Si_3 type — hexagonal — D_{6h}^3 — $P\,6_3/mcm$			$Z = 2$			
Ti_5Si_3 a = 7.465 (6)				$4M_I$ in (d)		
c = 5.162				$4M_{II}$ in (g)	$x_{Mn} = 0.23$	
				4Si in (g)	$x_{Si} = 0.60$	
Zr_5Si_3 a = 7.958 (33)						
c = 5.564						
Cr_3Si_3 type — tetragonal — D_{4h}^{19} — $I\,4/mcm$			$Z = 4$			
V_3Si_3 a = 9.42$_6$ (18)				$4M_I$ in (b)		
c = 4.75$_5$				$16M_{II}$ in (k)	$x_{Cr} = 0.075$	
Nb_3Si_3 a = 10.01$_5$ (18)					$y_{Cr} = 0.224$	
c = 5.07$_2$				4Si in (a)		
Ta_3Si_3 a = 9.8$_6$ (18)				8Si in (h)	$x_{Si} = 0.165$	
c = 5.0$_2$						
Cr_3Si_3 a = 9.170 (28)						
c = 4.636						
Mo_3Si_3 a = 9.642 (28)	9.617 (31)	9.66 (21)				
c = 4.905	4.899	4.99				
W_3Si_3 a = 9.605 (28)	9.645 (31)	9.56 (21)				
c = 4.964	4.969	4.94				
C_3B_3 type — tetragonal — D_{4h}^{20} — $I4/mcm$			$Z = 4$			
Nb_3Si_3 a = 6.57$_6$ (22)				4M in (c)		
c = 11.88$_7$				16M in (l)	$x_{Nb} = 0.166$	$z_{Nb} = 0.15$
				4Si in (a)		
Ta_3Si_3 a = 6.51$_6$ (22)				8Si in (h)	$x = 0.37_5$	
c = 11.87$_2$						
$CuAl_2$ type — tetragonal — D_{4h}^{18} — $I4/mcm$			$Z = 4$			
Zr_2Si a = 6.599 (11)				8M in (h)	$x_{Ta} = 1/6$	
c = 5.298				4Si in (a)		
Ta_2Si a = 6.157 (24)						
c = 5.03$_3$						
"β-W" type — (W_3O) cubic — O_h^8 — $Pm3n$			$Z = 2$			
V_3Si a = 4.721 (20)				6M in (c)		
				2Si in (a)		
Cr_3Si a = 4.564 (26)						
Mo_3Si a = 4.890 (32)						
$Ta_{11}Si$ — hexagonal, ideal Ni_3Sn type. $Ta_8(Ta_{0.25}Si_{0.75})$ (24)						
a = 6.10$_5$ for Ni_3Sn type - D_{6h}^4 — $P\,6_3/mmc$			$Z = 2$			
c = 4.91$_8$				2Sn in (c)		
				6Ni in (h)	$x_{Ta} = 0.826$	

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Technical Review

Review of Articles on Luminescence for 1955-1956[1]

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There have been two international symposia on luminescence. The papers delivered at the Cambridge meeting in April 1954 were published in a special supplement (1); those given at the Paris meeting in May 1956 were published in a journal (2) and also as a book (3). Papers of a general nature have been published by Henderson (4), Strange (5), McKeag (6), and Leverenz (7).

Oxygen-Dominated Phosphors

Preparation

There are several new phosphors. Rothschild describes a BPO_4:Tl, vanadates of five divalent elements, a chloroarseno-apatite activated with Pb and Mn, and a fluoroarsenate with Sb and Mn (8). Terol and Ward found that perovskite type oxides of La and Al are activated by Pr, Sm, and Eu (9). A phosphor of Sb_2O_3:Mn has been found to fluoresce in the deep red: Bernard and Janin obtained it directly (10); Kotera and Sekine found that B_2O_3 enhanced its luminescence and that it contains some Sb_2O_4 (11). Larach and Shrader prepared a BN phosphor whose multiband emission extends from 2950Å to 6500Å, under excitation by u.v., cathode rays, and a-c fields (12).

Three investigations deal with new pyrophosphates. Kinney found that the emission of $Ca_2P_2O_7$:Sb at 4150Å is greatly enhanced by the presence of Na_2O to compensate for valence differences, and that the Sb sensitizes a Mn band at 5750Å (13). Ranby, *et al.*, studied the structure and luminescence of (Ca,Ba,Sr)$_2P_2O_7$ with primary activation by Sn emitting at 4600Å, and by Ce emitting in the u.v., to sensitize Mn emission in the range 4800-6150Å (14). McKeag and Steward prepared Sn-activated pyro- and tetraphosphates of Sr and Ba whose luminescence ranged from blue to red depending on composition and firing temperature; they found also that the presence of Li in Zn_2SiO_4:Mn introduced a secondary band at 6400Å and that its use in (Ba,Sr)$_2SiO_4$:Ce:Mn gave red emission under 3650Å, useful for color correction in the high pressure mercury lamp (15).

Calcium halophosphates have been extensively studied. There is a general paper by Doherty and Harrison (16). A highly detailed study by means of differential thermal analysis was made by Wanmaker, *et al.*, of the various reactions involved in their preparation; their course at various temperatures was followed by x-ray tests (17). Ouweltjes and Wanmaker (18) and Wanmaker (19) tell of the effects produced by altering the proportions of ingredients, and the latter discusses how an SbO group may be substituted for a CaF group. Somewhat related is the description by Wollentin of substitutions in the cadmium fluoroapatites (20).

Phase equilibria have now been well established by Hummel, *et al.*, for two borate systems, that of CdO-B_2O_3 with its four compounds (21), and that of ZnO-B_2O_3 with two compounds (22).

From studies on the preparation of ZnO phosphors, Riehl and Ortmann ascribe its green luminescence to oxygen vacancies (23). Tungstates of the alkaline earth metals were made by Gobrecht and Weiss under activation by uranium; there was a uniform red band common to all and a green band whose spectral location depended on the cationic environment (24). Sulfates and silicates of the alkaline earth metals were found by Kotera to respond to activation by a variety of oxyacid groups (25). Kotera with Sekine has also studied the fluorescence of the unactivated vanadates of the divalent metals as well as the aluminates activated with Mn (26).

Properties

Among the silicate phosphors there are two studies on a magnesium fluorosilicate activated with low Ti to emit at 5430Å; the Ti serves also to sensitize a double band Mn emission at 5430Å and 6100Å. In addition, Dziergwa and Panke make note of its very slow decay (27), and Ranby and Henderson cite its lamp efficiency as 58 lpw with Ti alone and 39 lpw with Mn as well (28). Of the two Mn bands in $CaSiO_3$:Pb:Mn, Lange shows that the 5600Å remains invariable in spectral location whereas the 6300Å is shifted to shorter wave length by increase in Mn or in temperature (29). As Dziergwa and Lange point out, this is in contrast to $ZnBeSiO_4$:Mn, each of whose bands is fixed in location but variable in intensity (30). The effect of Sr in favoring the 6300Å band in $CaSiO_3$:Pb:Mn is shown by Lange and Kressin to be due to a de-

[1] This review, written in February 1957, covers those articles published in English, German, and French that have come to the writer's attention since the previous review, published in *This Journal*, **102**, 129C (1955).

crease in the proportion of the luminescent alpha form with a resulting increase in the effective concentration of Mn (31).

From studies of the apatite phosphors, Fonda finds that the emission bands of haloarsenates, as well as of zinc arsenate, lie at longer wave length than in their phosphate homologues (32); and that the transfer of excited energy from sensitizer to activator in the halophosphates suffers less loss in a single transfer step than after a succession of steps (33). In contrast, Ouweltjes finds that the presence of Mn raises rather than lowers the net quantum efficiency, and he believes that losses may be due to absorption of excitation energy rather than to nonradiative effects (34). Thurnau finds that the halophosphates and five other common phosphors are also excited in the far u.v. within the range of 1000-1640Å to an extent that decreases with wave length to a minimum and then may increase; the most efficient was $Zn_3(PO_4)_2$:Mn (35).

In tests on miscellaneous phosphors, Vlam found that the emission bands of $CaWO_4$:Pb, Zn_2SiO_4:Mn and $(Zn,Be)_2SiO_4$:Mn either follow or may be resolved into Gaussian forms (36). Absorption and emission measurements of Runciman on Bi-activated oxides at 77°K fit the Ewles equation; he suggests the electronic states that may be involved (37). The decay of the u.v. and green emission bands of ZnO:Zn has been measured by Gobrecht, *et al.*, at a variety of temperatures; the results denote a different mechanism of luminescence than in the sulfides (38). Nishikawa, *et al.*, found that an afterglow from $CaWO_4$ appeared after firing with excess CaO but at a loss in fluorescence (39). The thermoluminescence of alkaline halides has been measured by Bose (40). Iwase has observed how the rare earths could be assimilated as activators by natural calcareous substances to give rise to cathodoluminescence on conversion to oxide (41). A reasonable explanation for "flame excitation" is offered, according to Hanle and Niermann, by the rise in luminescence of heated phosphors under excitation by active H or N; this is ascribed to the removal of an adsorbed film of gas with consequent opportunity for more direct excitation of the phosphor surface by the energy released on recombination of the activated gas atoms (42).

Mechanism

Many papers deal directly with the character of the luminescence center. According to Schulman, data on the temperature dependence of efficiency, decay, absorption, and emission serve to elucidate dissipative transitions and energy transfers, and to allow calculation of configurational coordinate curves (43). This conception is applied by Klick to Mn emission (44). According to a criterion set up by Dexter, *et al.*, luminescence can occur only when the crossover to the ground electronic state is at a higher energy level than that attained in excitation (45). A general theory of localized activator systems is discussed by Williams and applied to KCl:Tl, KCl:Mn, MgO:Mn^{++}, and ZnS phosphors (46). Uncertainty is cast on these calculations in the opinion of Knox and Dexter by the failure to predict the correct ratio of oscillator strengths for two of the absorption bands in KCl:Tl (47). On the basis of emission and excitation spectra for NH_4Br:Tl and KCl:Tl, Butler assigns energy levels which differ somewhat from those of Williams for KCl:Tl (48). There is an alteration in emission and conductivity of unactivated, monovalent halides produced by thermal or mechanical shock or by introduction of divalent ions; this is ascribed by Ewles and Stead to the formation of ion vacancies which become essential parts of the luminescence center (49). Charge compensation may be secured by such vacancies as well as by the presence of ions of a different valency, and Runciman discusses their localization within the luminescence center and their application to sensitized luminescence and to the occurrence of multiple band emission (50). He makes a further application to NaF:U phosphors on the basis of their fluorescence and absorption spectra at low temperature and of their impurity content (51). From decay and glow curves of NaCl:Ag and $CaSO_4$:Mn, Lepper has discussed their simultaneous emission of luminescence and of electrons (52). Gruen, *et al.*, describe the luminescence of $LaCl_3$:Eu and its relation to color centers formed by gamma irradiation (53). Klick failed to find any appreciable photoluminescence from LiF and KCl treated to form color centers (54).

Bernard and Janin have studied the double band emission of $CaSb_2O_6$:Bi and find that the 4850Å band is reduced relatively to the 4600Å by increase in Bi or in temperature, ascribing it to the cluster theory (55). Runciman discusses the electronic transitions that may be responsible for the fine structure of Bi-activated oxide phosphors (56). A note of warning is given by Hershberger concerning measurements of paramagnetism; the signals that he observed with ZnF_2:Mn, Zn_2SiO_4:Mn, ZnS:Mn, and ZnS:Cu and other phosphors he attributes to photoconduction rather than to a change in multiplicity of the Mn ion (57).

Sulfide Phosphors

Properties

Kroeger has given a broad review of the absorption and emission characteristics of ZnS phosphors as related to composition, structure, and preparation (58). Addamiano finds luminescence from ZnS:Zn after firing at 650°-800°C without flux, although lower than at higher temperature and much lower than with fluxes (59). According to Rothschild and Eaton, the absorption of ZnS:Ag and of CdS:Ag is shifted to longer wave length with a NaCl flux and to still longer with $BaCl_2$ (60). Van Doorn finds that the absorption edge of ZnS single crystals is shifted from 3340Å at 77°K to 3970Å at 878°K at a rate that increases with temperature (61). The effects of the intensity and wave length of excitation on the quantum efficiency have been measured and discussed by Antonov-Romanovsky (62), and a broad treatment of nonlinear behavior has been given by Duboc (63). Grillot and Bancier-Grillot describe the use of radioactive tracers in controlling the purification of ZnS phosphors (64).

The killer effect of Fe on the blue band of ZnS:

Ag is accompanied by a red emission band due to Fe, according to Gergely (65). In addition to the killer effect, Arpiarian has observed an intensifying effect of Fe and Co at low concentration on the luminescence of ZnS:Au and ascribes it to displacements of the Fermi level that accompany changes in their concentration (66). From tests by Shionoya, the suppression of Cu emission in ZnS:Cu:Mn in favor of the Mn band is not an evidence of the Schoen-Klasens effect but denotes a direct transfer of excitation energy, for in the presence of Cu or Pb, the Mn emission band appears when irradiated in their excitation bands as well as in its own (67).

In the precipitation of ZnS from chloride or sulfate solutions, Palumbo and Levine find a persistent contamination of sulfate due to surface adsorption, and of chloride due to volume adsorption as well as surface (68). A photoenhanced adsorption of oxygen was observed by Kobayashi and Kawaji when ZnS:Cu was irradiated within its absorption band (69), an effect similar to Hedvall's observation that the adsorption of dyes by ZnS phosphors was enhanced under photoexcitation.

In sulfide derivatives, Larach found that the emission of ZnSe phosphors is found at longer wave lengths than in ZnS, an accompaniment of the larger ionic size of Se compared to S (70). A similar effect was found by Larach, *et al.*, in the cathodoluminescence of Zn(S, Te) phosphors containing up to 8% ZnTe, the solubility limit of Te; in general, Te, again of larger ionic size than S, shifted the emission to longer wave lengths and served also to produce self-activation in the absence of chloride (71). Jaffe and Banks confirm Brauer's conclusion that the band emission of Eu in the alkaline earth sulfides is due to Eu^{2+} and the line emission in the oxides is due to Eu^{3+}. In addition they find that band emission may be produced in some oxides by hydrogen firing. The band emission is ascribed to the outer electron shell and the line emission to the inner shell, protected from the atomic environment (72).

Mechanism

Considerable attention was given to the role of traps. Tolstoi presents and discusses results from two novel methods for measuring buildup and decay, with evidence that conductivity arises from a quasi-band of localized electronic levels (73). Kallman and Spruch have also studied buildup and decay but under excitation by high energy particles; they discuss the matter of traps and stimulation (74). A theoretical treatment of decay is given by Lehovec from consideration that an activator center, while still filled, may serve as a trap for a conduction electron (75). A similar view is expressed more extensively by Curie, who concludes that traps localized in the vicinity of centers are the basis of monomolecular decay, in contrast to those so independently located that they give rise to bimolecular decay (76). Thermoluminescence tests by Neumark, *et al.*, fail to show evidence of surface traps (77); but Riehl and Ortmann point out that there are some traps so shallow that they can be detected only at −210°C (78). Highly significant discussions, with models, on the quenching and stimulation of photoconductivity and luminescence are given by Bube (79), Matossi (80), and Kallmann (81). Tests on 30 phosphors by Gobrecht, *et al.*, developed photoconductivity only for the sulfides, not for oxygen-dominated phosphors; glow curve peaks for both conduction and luminescence were closely adjacent (82). The alkaline metal polysulfides of these investigators showed an exponential decay whose rate increased with temperature (83).

In regard to the character of luminescence centers, Bowers and Melamed have found an absence of paramagnesium in unexcited ZnS:Cu, with and without chlorine and containing up to 0.1 mole % Cu with fluorescence in the blue, green, and red. They conclude that the blue band must be ascribed to Zn^{2+} vacancies, the green to substitutional $Cu^{+}Cl^{-}$, and the red to interstitial Cu^{+} (84). The same result was found by Grillot, who attributes the green band to an oxygen replacement next to a copper ion; he finds two emission bands for CdS:Ag as well as for CdS:Cu, comparable with the two bands in ZnS:Cu (85). Larach and Turkevich were also unable to detect paramagnetism in ZnS:Ag and in various forms of ZnS and CdS; the increase in diamagnetism produced by Cl and Al suggested lattice perturbations (86). In tests by Oshima and Nagano, excitation of ZnS:Mn developed a very weak paramagnetism which increased with Mn content even above the quenching concentration, but was insufficient to denote any appreciable change in the multiplicity of Mn centers (87). Riehl and Ortmann found that fluorescence results on partial desulfurization of ZnS:Cu in absence of halides and trivalent elements and conclude that it arises from vicinity of copper ions to sulfur vacancies (88). In an exhaustive treatment of this matter, Prener and Williams conclude that luminescence arises from an association of activator and coactivator as second or third nearest neighbors (89). Schulman and Klick question this view and consider that the absence of luminescence found by Prener and Williams in ZnS containing Cu^{65} derived from Zn^{65} is due to its presence as nonluminous Cu^{2+} rather than Cu^{+} (90).

Conjectures have been made concerning changes in the energy band model. Garlick relates the information on absorption, excitation, and energy storage to the accepted model (91), and a review and discussion of it in its conventional form are presented by Schoen (92). Other papers deal with observations that denote a need for radical modifications or additions to the model. Luminescence and conductivity measurements by Hamilton on single crystals of ZnS:Cu denote that lattice irregularities or Cu_2S groups may be electron donors as well as the luminescence centers (93). As to other possible transitions, Garlick has measured *IR* bands which he ascribes to transitions between activator levels and the filled band (94). Broser and Broser-Warminsky have investigated the emission, absorption, stimulation, and quenching spectra of single crystals of ZnS and CdS and propose an energy model with several novel features, including two levels for an unexcited activator (95). As another radical change,

Lambe, *et al.*, have proposed that holes are the charge carriers in conduction and that emission occurs by recombination of a free hole in the valence band with an excited electron caught in a shallow trap; they discuss its bearing on the buildup, decay, and quenching of luminescence and photoconductivity (96). Their theory is favored by experiments of Smith and Turkevich on neutron bombardment of ZnS:Cu (97). In experiments by Halsted, however, on films of sulfides in a d-c field, maximum luminescence occurred when the positive electrode was irradiated with u.v., demonstrating that electrons rather than holes are the charge carriers (98).

Cathodoluminescence

Phosphor Characteristics

A review is given by Garlick of present experiments on the fundamental processes involved, such as excitation, secondary electron emission, and scattering (99). A review by Hill covers the characteristics of notable phosphors (100). Bril and Klasens discuss the efficiencies and spectral distribution of various phosphors suitable for the tricolor TV tube (101). Changes in spectral distribution of sulfide phosphors after settling and heating are given by Bachman, *et al.* (102). Studer and Cusano describe the preparation and properties of transparent screens of ZnS activated with different elements (103). Iwase relates the performance of Sm and Pr in Al_2O_3 to the latter's three prototypes (104). In tests by Saksena and Pant, the emission band of the alkaline halides free of added impurity was shifted to longer wave lengths by increase in ionic size of either the metal or halogen ion (105). Koller shows that the brightness of various phosphors in 120 v CR lamps increases in the order of decreasing voltage drop, Zn_2SiO_4:Mn, ZnS:Zn, ZnO:Zn (106).

Deterioration

Several papers deal with the importance of the secondary emission ratio in determining the potential of a screen and thereby its characteristics. When the ratio is less than 1, de Gier, *et al.*, demonstrate that the screen potential falls below that of the anode, lowering the screen brightness and forming positive ions to bombard the screen and deteriorate it; the ratio is raised by a film of MgO on the screen (107). According to Dowling and Sewell, contamination with organic vapor is injurious because it lowers the ratio (108). This is confirmed by Rottgardt and Berthold, who failed, however, to find the use of oil diffusion pumps injurious (109). As Rottgardt, *et al.*, demonstrate, the sticking potential, that accompanies a ratio less than 1, falls to lower voltage with life of the tube and is raised temporarily by introduction of H (110). Laponsky, *et al.*, confirm these observations, but point out that the sticking potential in practice is merely a discontinuity due to roughness of screen surface or to incomplete covering of the glass; they discuss also its relation to x-burns (111).

The effect of positive ions in producing this burn has been studied intensely. According to Berthold, the injury done by H can be partially restored by bombardment with electrons (112). Young measured the injury done by H and five other gases; he found that it was greater for ZnS:Ag than for Zn_2SiO_4:Mn, and could be annealed out above 450°C (113). Gilfrich measured it with H ions for 13 phosphors and found that the rate of deterioration of ZnS:Ag was much greater than that of $(Zn, Be)_2SiO_4$:Mn but was decreased in ZnS phosphors by a change from hexagonal to cubic structure and by partial substitution of Se or Cd; it was also much less for ZnS:Mn (114).

Rottgardt and Berthold have found that the normal deterioration of aluminized screens of ZnS:Ag depends on the number of bombarding electrons and not on their voltage and, again, that it is less for cubic than for hexagonal ZnS (115).

Electroluminescence

The many papers fall into five groups. The first deals with general characteristics of ZnS cells. Tests on the brightness waves as related to different conditions of voltage and frequency are offered by Destriau (116), Luyckx (117), Gobrecht, *et al.* (118), Lehmann (119), Harman and Rehbold (120), Matossi and Nudelman (121), Schwertz, *et al.* (122), and Alexander, *et al.* (123). The effect of temperature has been studied by Mattler (124). For ZnS:Cu he found the same spectral shift from blue to yellow on increase in temperature that had been observed by Waymouth and Bitter (125) under the same conditions as well as after prolonged maintenance of a d-c field; this is ascribed to the Schoen-Klasens effect. Smith obtained both edge and visible emission from pure ZnS single crystals (126). General reviews are given by Destriau and Ivey (156), Piper (127), and Fischer (128). In single crystals of ZnS coated with Cu, Diemer found that the application of a field produced diffusion of Cu and developed light patterns as lines in the direction of crystal growth, lines that may represent internal barriers of extremely high field strength; there were also uniformly oriented black dendrites (129). Bontinek and Dekeyser observed formation of the latter when excess Zn or Ag was introduced (130).

The second group discusses possible mechanisms of operation. Many investigators believe that the key to luminescence from phosphor grains lies in a unique surface phase which builds up such a high field strength that electrons, which are released to the conduction band, acquire sufficient energy to excite the activator levels. The constitution of this phase is cited by Williams, *et al.*, to be simply a barrier exhaustion layer (131). Others give it a specific chemical composition. Zalm and Diemer, *et al.*, believe it to be associated with a film of Cu_2S (132), as suggested by the observations of Diemer (129) and of Frankl (133) on single crystals; Butler and Waymouth ascribe it to CuO, CuS, ZnO, or simply a localized high concentration of Cu (134). Whereas these investigators consider that luminescence is restricted to the surface of grains, Destriau contends that in his cell it is a volume effect (116).

Thornton has constructed cells of dry compressed powdered phosphors and develops a theory into which their characteristics fit (135). From tests on

single crystals at various temperatures, Alfrey and Taylor (136) propose modifications to Williams' theory (131), and Short, *et al.*, show that luminescence may be associated with one-dimensional disorder (137).

Electrothermo-luminescence denotes the light emanations that appear on warming from a low temperature. Its maxima are close to those for glow curves and are associated likewise with the release of electrons from traps. In addition to studies by Hahn (138) and Freund (139), Neumark has observed corresponding variations in conductivity as well (140).

Photo-electroluminescence is the term given a new phenomenon by Cusano and Williams. They have developed a light amplifying device based on a film of ZnS:Mn. Under application of an a-c or d-c field and irradiation by u.v. or x-ray, there is a light emission manyfold greater than that resulting from either form of excitation alone. Whereas electroluminescence is ascribed to the creation of charge carriers by field ionization of deep donor levels in an exhaustion layer on the cathode side, in this case their creation depends on photon absorption (141). There are evidences of related phenomena. The variations in photoluminescence on application of a field are described by Matossi and Nudelman (142), Gumlich (143), and Gobrecht and Gumlich (144). The same effect under x-ray excitation, as first observed by Destriau, has been studied further by Destriau, *et al.* (145).

Compounds other than the sulfides have been found to exhibit electroluminescence. Szigeti, *et al.*, demonstrate that C is the activator in SiC crystals (146). Wolff, *et al.*, found an orange emission band in GaP which they assigned to an excess of Ga, and a red band due to Zn (147). Larach and Shrader measured complex spectra from BN (148).

Diemer, *et al.*, have devised an image-intensifying screen by superimposing an electroluminescent cell of ZnS:Cu over a photoconducting layer of CdS:Cu (149).

Miscellaneous

Studies have been continued on the alkaline halide phosphors as scintillation counters and as dosimeters by Dobrinski and Hinrichs (150), and by Mandeville and Albrecht (151). Consideration has also been given by Smidt (152) and by Koontz, *et al.* (153) to the characteristics of ZnS:Ag under excitation by high energy particles.

Waymouth and Bitter offer an analysis for the properties of the plasma in the fluorescent lamp and apply it to lamp characteristics (154). From experiments with radioactive Hg as a tracer, Burns and Kastner conclude that there is no relation between the depreciation of lamps and the amount of Hg tightly held on the tube walls. (155).

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1958 JOURNAL.

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December 1957 Discussion Section

A Discussion Section, covering papers published in the January—June 1957 JOURNALS, is scheduled for publication in the December 1957 issue. Any discussion which did not reach the Editor in time for inclusion in the June 1957 Discussion Section will be included in the December 1957 issue.

Those who plan to contribute remarks for this Discussion Section should submit their comments or questions in triplicate to the Managing Editor of the JOURNAL, 216 W. 102 St., New York 25, N. Y., *not later than September 1, 1957*. All discussion will be forwarded to the author, or authors, for reply before being printed in the JOURNAL.

Technical Feature

Hydroelectric Power in Quebec and the Atlantic Provinces

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Electric utilities and electrochemical and electrometallurgical industries in Quebec have always worked together to their mutual advantage. As early as 1890, an electrolytic $KClO_3$ plant was established in Buckingham. In 1901, Canada's first aluminum smelter started operation at Shawinigan Falls. In the same year, The Shawinigan Carbide Co., which has since become Shawinigan Chemicals Limited, was formed. Besides Al and CaC_2, Shawinigan Falls now produces silicon carbide, caustic soda, electric steel, and many other products and derivatives. The new electrochemical center recently started by The Shawinigan Water and Power Co. at Varennes is also assured of a great future.

With the development of 1,408,000 hp at Beauharnois, from 1931 to 1954, the region became another center of electrochemical production. Here can be found ferroalloy, Al, and chlorine caustic soda plants.

With the gradual harnessing of the now available 2,800,000 hp in the Saguenay region, one of the largest Al smelters in the world was developed with an annual capacity of about 500,000 tons. The production of aluminum requires some 24,000 kwhr/ton of product and about 1,000,000 kwhr/man/year.

The four Atlantic provinces, with the possible exception of Newfoundland, have not been as favored with hydraulic resources as Quebec. This explains why that region has so far seen very little development of the electrochemical and electrometallurgical industries. Whenever the potential of 4,000,000 hp at Grand Falls, on the Hamilton River, is harnessed, important electrothermal industries will surely be attracted wherever the power will be utilized.

The following 12 charts bring out the most pertinent facts relating to the hydroelectric industry of Quebec and the Atlantic Provinces and some of the aspects of the electrochemical and electrometallurgical industries. The highlights revealed by these charts follows:

1. The harnessing of hydroelectric power in Quebec has had a great influence on the industrial development of the province. It should have an even greater influence in the future, as more mineral resources are exploited and the development of power is further accelerated.

2. The policy of conservation of the water power resources of Quebec, which has been followed throughout the evolution of the industry, has been responsible for the low cost of electricity.

3. The Atlantic provinces, with the exclusion of Newfoundland, have not been as favored with hydroelectric power resources as Quebec. The future development of the Hamilton River, in Newfoundland, will probably attract numerous electrometallurgical industries wherever the power will be used.

4. The province of Quebec has the greatest wealth of hydroelectric power in Canada. British Columbia comes next, then Ontario. With the development of 1,100,000 hp in the St. Lawrence River now proceeding, Ontario will have used most of its water power resources. Quebec and British Columbia, more favored in this regard, will have additional hydraulic resources to exploit for some years to come.

5. Quebec leads the world with a production of electricity of 8,100 kwhr per capita. In comparison, Norway's consumption in 1954 stood at 6,300 kwhr, the United States at 3,400 kwhr, the United Kingdom at 1,450, France at 1,000, and the U.S.S.R. at only 700 kwhr.

6. Exports of wood and paper and nonferrous metal industries are responsible for the unusually high production of electricity in Quebec. The development of additional electrochemical and electrometallurgical industries will further increase the per capita requirements of electricity.

7. The pattern of utilization of electricity in the Atlantic provinces is very different from Quebec. Moreover, it is different in each of the constituent provinces. Except for Nova Scotia, the contribution of electrochemical and electrometallurgical industries to the Canadian production is practically nonexistent.

8. Of all electrometallurgical processes, the production of Al requires the largest volume of electricity. In comparison, the smelting of Zn, Fe, and Cu ore requires only about ⅛ as much.

9. The Al industry in Quebec started in 1898; it has now grown into a giant of modern industry having an annual capacity of over 540,000 tons, or nearly ⅛ the total capacity in North America.

10. The volume and value of the Canadian metallic mineral production in 1954 was at an all-time

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high. Ontario led with 51% of the total value, Quebec and British Columbia followed with 16% each. The Prairies contributed 8%, the Atlantic provinces about 5%, and the Yukon and Northwest Territories 3%.

11. The rapidly growing production of Cu and Zn in Quebec and the production of Fe ore should favor the further development of its electrometallurgical industries.

12. The 1,000,000-ton capacity of electric steel furnaces in Canada in 1954 was about three times the capacity in 1939 but only 20% higher than the capacity at the peak of World War II activities, in 1944.

Conclusions

Important additional sources of low-cost hydroelectric power will continue to attract electrothermal industries to Quebec. It is very important, however, for the greatest benefit of the whole population, that an increasing part of that power be directed to industries employing the greatest possible number of people.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1958 JOURNAL.

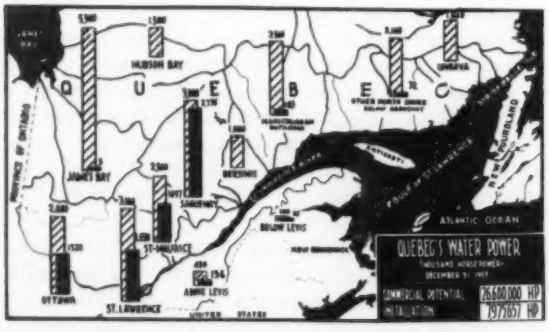

Fig. 1. Water power in Quebec. Quebec's water potential, at ordinary six-month flow, amounts to 20,445,000 hp and, at 130% of six-month flow, on the basis of actual installation amounts to 26,600,000 hp. About half of that power lies within economic transmission distance of Montreal.

At the end of 1955, the hydraulic turbine installation stood at 7,975,697 hp, of which 7,569,853 hp were developed for sale by electric utilities and 405,804 hp were developed for their own use by pulp and paper mills (350,344 hp) and other industries (55,460 hp).

So far, the development of water power has been limited to the most accessible rivers; the Saguenay has an installation of 2,776,000 hp, the St. Maurice 1,697,000 hp, the St. Lawrence 1,658,000 hp, and the Ottawa 1,342,000 hp.

Twelve producers have installations of more than 50,000 hp. The Aluminum Co. of Canada Limited leads with 2,040,000 hp, Hydro-Quebec is second with 1,746,000 hp, and the Shawinigan company third with 1,720,000 hp. The Gatineau Power Co. and the Saguenay Power Co. have respective installations of 682,500 and 543,000 hp.

Heading Quebec's 16 plants of more than 150,000-hp capacity are Beauharnois with 1,408,000 hp, followed by Shipshaw with 1,200,000 hp, and Isle Maligne with 540,000 hp. Of the remaining 13 plants, seven are on the St. Maurice river, three in the Saguenay basin, two in the Ottawa basin, and one on the St. Lawrence.

The capacity of the hydroelectric plants under way or ready for construction in the next four years amounts to 1,735,000 hp, as follows:

1956	Bersimis #1	Hydro-Quebec	450,000 hp
	Upper Ottawa	Hydro-Quebec	16,000
	Gatineau	Gatineau Power Co.	47,000
			513,000
1957	Bersimis #1	Hydro-Quebec	450,000
	Manicouagan	Manicouagan Power Co.	150,000
	Chicoutimi	Eastern Smelting & Refining Co.	42,000
			642,000
1958	Bersimis #1	Hydro-Quebec	300,000
	St. Maurice	The Shawinigan Water & Power Co.	140,000
			440,000
1959	St. Maurice	The S. W. & P. Co.	140,000
	Bersimis #2	Hydro-Quebec	300,000*
			440,000*

* Estimate

Whereas, between 1945 and 1955, the hydraulic turbine installation in Quebec grew at an average yearly rate of 213,000 hp, the last five years saw a yearly growth of 320,000 hp. The average yearly growth of the next four years will presumably amount to some 500,000 hp. At that rate, it will not take long before the remaining water power potential of Central Quebec is absorbed.

So far, the utilization of the water power resources of Quebec has had a great influence on its industrial development. This influence will be accrued as the utilization is accelerated.

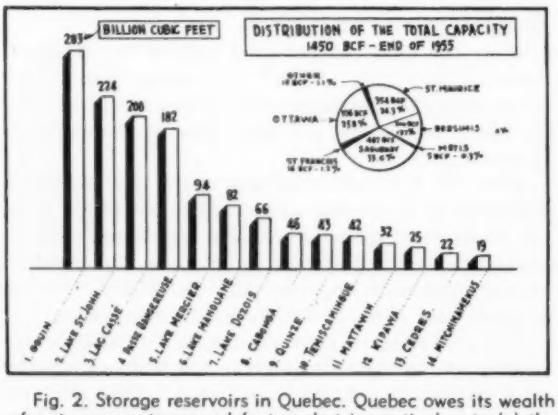

Fig. 2. Storage reservoirs in Quebec. Quebec owes its wealth of water power to several factors, but in particular, to (a) the Canadian Shield with its innumerable waterfalls, (b) a large body of fresh water, (c) a high and exceptionally stable yearly and monthly precipitation, and (d) a policy of conservation which has been responsible for the development of the numerous storage reservoirs now to be found throughout the basins of the most important rivers of the province.

The elevation of the land (1,400 ft) separating the Arctic and the James Bay basins from the St. Lawrence watershed is fairly even from Ungava to Ontario. The drop to the St. Lawrence offers many opportunities for the development of power. For example, nine power sites with a total head of over 1,000 ft are found on the St. Maurice River alone; six of them have already been developed to produce 1,700,000 hp and plans are under way for the development of another site which will have a capacity of 330,000 hp.

Quebec's total area of 595,000 square miles contains 71,000 square miles of fresh water. In comparison, Ontario's fresh water area, which includes half the surface of the Great Lakes, amounts to only 64,441 square miles. The Northwest Territories have 51,500 square miles of fresh water area, Saskatchewan 31,500, and Manitoba 26,800 square miles.

Precipitation in Montreal is fairly representative of the precipitation over the province. Averaging about 41 in., it is nearly 30% higher than that of Toronto at 32 in. and 86% higher than the 22-in. precipitation of Winnipeg. It is, however, 28% less than Vancouver's 57 in. and very differently distributed over the year.

Whereas the average monthly precipitation in Vancouver reaches as much as 9 in. in November, December, and January, and as little as 1 in. in July, the average monthly precipitation in Montreal fluctuates only between 3.75 in. in January and July and 2.60 in. in April.

Quebec's storage reservoirs contain 1,450 billion cubic feet of water, or enough to fill a reservoir about one cubic mile. These reservoirs help gather in the spring the water from the 100 in. of snow which normally fall over the entire watershed during the winter months, together with the additional run-off that obtains. The benefits derived from these storages have been incalculable; on the St. Maurice River alone it is estimated that it has transformed the potential of the river from about 700,000 hp, under natural conditions, to about 2,500,000 hp under present regulation.

Were it not for these storage reservoirs, the extraordinarily low revenue obtained from the sale of each kilowatthour would never be possible.

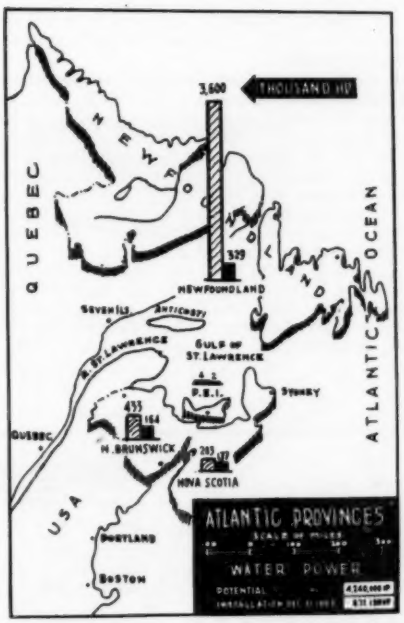

Fig. 3. Water power in the Atlantic Provinces. Water power in the Atlantic provinces has been estimated conservatively at some 4,240,000 hp, that is, 3,600,000 hp in Newfoundland, 433,000 hp in New Brunswick, and 203,000 hp in Nova Scotia. A recent survey of the power potential of the Hamilton river in Labrador indicates a potentiality of some 4,000,000 hp, which exceeds what was previously assumed to be available.

So far, 672,180 hp of the Atlantic provinces' water power resources have been harnessed, as indicated above, 429,924 hp for sale by electric utilities, and 242,256 hp, for their own use, by pulp and paper mills (216,509 hp), and other industries (25,747 hp).

Hydroelectric power constitutes 58% of all power installations in the Atlantic provinces. It amounts to 98% in Newfoundland, 55% in New Brunswick, 36% in Nova Scotia, and practically does not exist in Prince Edward Island.

At the end of 1955, the principal hydroelectric power producers in the Atlantic provinces were: Bowaters Limited (156,000 hp) in Newfoundland, the Nova Scotia Power Commission (103,940 hp), the Anglo-Newfoundland Development Co. (84,900 hp), the Gatineau Power Co. (80,000 hp), the Newfoundland Light & Power Co. (55,000 hp), and the New Brunswick Electric Power Commission (38,000 hp). Figures in parenthesis represent the total capacity of all the plants producing 2,000 hp and over.

The Deer Lake 250-ft-head development operated by Bowaters Limited on the Humber river in Newfoundland, with its installation of 156,000 hp, is the leading plant of the Atlantic provinces. Grand Falls 132-ft development on the St. John river in New Brunswick follows with 80,000 hp. Grand Falls 109-ft development on the Exploits River in Newfoundland comes third with 64,000 hp capacity.

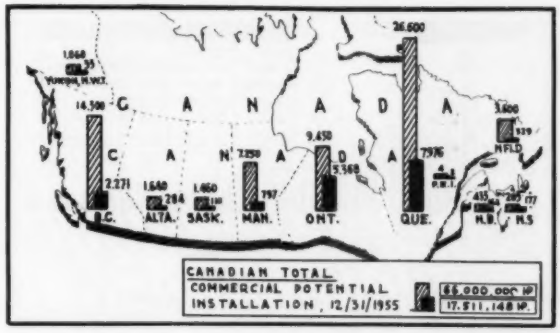

Fig. 4. Water power in Canada. The most recent information available (March 15, 1956) reveals Canada's power commercial potential (130% of indicated six-month flow power) to be 66,000,000 hp and its distribution as indicated in the above chart.

Quebec's potential of 26.6 million hp represents about 40% of the total, British Columbia's 14.3 million hp 22%, the Prairies' and Northwest Territories' 11.4 million hp 17%, Ontario's 9.5 million hp 15%, and the Atlantic provinces' 4.2 million hp 6%.

At the end of 1955, Canada's total hydraulic turbine installation stood at 17,511,148 hp. Quebec led the provinces with 7,976,000 hp or 46% of the total. Ontario came second with 5,368,000 hp, and British Columbia third with 2,271,000 hp. The Prairie provinces had 1,191,000 hp and the Atlantic provinces 672,000 hp.

The St. Lawrence (including Niagara) was Canada's most utilized river with 4,150,000 hp of hydraulic turbine installation: 1,600,000 hp in the Beauharnois-Cedars section in Quebec and about 2,560,000 hp on the Ontario side of the Niagara. The installation in the Saguenay basin amounted to 2,800,000 hp, that in the Ottawa basin to 2,670,000 hp—about evenly divided between Ontario and Quebec—and that in the St. Maurice basin to about 1,700,000 hp.

The Sir Adam Beck 1,820,000-hp plant is the leader among Canadian power plants; the Beauharnois 1,408,000-hp plant of Hydro-Quebec is second, and Shipsaw 1,200,000-hp plant, belonging to the Aluminum Co. of Canada, Ltd., on the Saguenay river, is third. In comparison, Grand Coulee in the United States has an installation of 2,630,000 hp, Hoover Dam, 1,670,000 hp, and Bonneville, 700,000 hp.

The Ontario Hydro is by far the largest hydroelectric power producer in Canada. Its 4,550,000-hp installation at the end of 1955 compared with the 2,490,000-hp installation of the Aluminum Co. of Canada. Other producers, with more than one million hp, were Hydro-Quebec with 1,746,000 hp and The Shawinigan Water and Power Co. with 1,720,000 hp. The British Columbia Electric Co. had 745,000 hp, Gatineau Power Co., 765,000 hp, the Consolidated Mining and Smelting Co., 625,000 hp, the Manitoba Hydro Electric Board, 587,000 hp, and Saguenay Power Co., 540,000 hp.

At the present time, developments through Canada for operation within the next four years total a capacity of around 4,750,000 hp, distributed as follows:

Regions	Additional Installations	Estimated total installations at end of 1959
	hp	hp
British Columbia and Yukon	1,170,000	3,440,000
Prairies	1,000	1,192,000
Ontario	1,437,000	6,800,000
Quebec	2,035,000	10,000,000
Atlantic provinces	101,000	773,000

By the end of 1959, the total hydraulic turbine installation in Canada will stand at around 22,200,000 hp, as compared with an installation of 17,511,000 hp at the end of 1955 and one of 12,563,000 hp at the end of 1950.

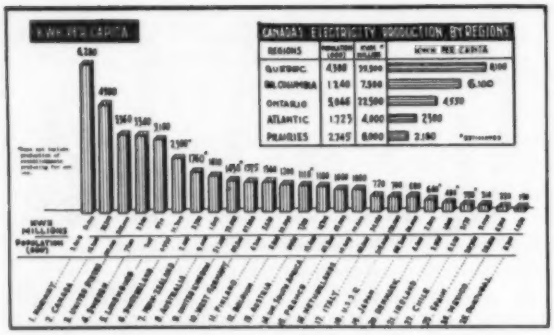

Fig. 5. World leading producers of electricity. In relation to its population, the province of Quebec is the leading electricity producing region of the world. Indeed, its production of 8,100 kwhr per capita in 1954 exceeded that of Norway (6,280 kwhr per capita) by 30%.

In Canada, Quebec's production exceeded the estimated 6,100, kwhr per capita of British Columbia by 33%. In comparison, the production of the other regions of the country was as follows: Ontario 4,550 kwhr, the Atlantic provinces 2,300 kwhr, and the Prairies 2,180 kwhr per capita.

Throughout the world, the production per capita in 1954 stood at 3,360 kwhr in the United States, 2,300 kwhr in Switzerland, 1,430 kwhr in the United Kingdom, 1,000 kwhr in France, and about 700 kwhr each in Italy, U.S.S.R., and Japan.

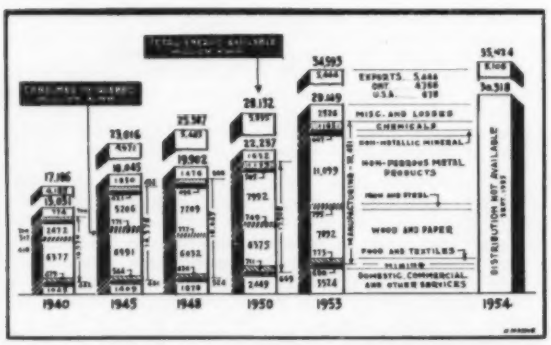

Fig. 6. Pattern of utilization of electricity in Quebec. Large exports of electric energy and the great energy requirements of the nonferrous metal and of the wood and paper industries account for the exceptionally high production of electricity in Quebec. This situation is well pictured above, detailing the utilization of electricity between 1940 and 1953.

In the last year for which complete information is available (1953), the utilization of the electricity produced in Quebec was proportionately distributed as follows:

Exports	15.70%	Iron and steel industries	2.30%
Domestic and other retail services	10.20	Nonferrous metal industries	32.10
Mining	1.97	Nonmetallic mineral industries	2.02
Food and textile industries	2.22	Chemical industries	3.37
Wood and paper industries	22.80	Unaccounted for	7.32

Exports, at all times, have represented a high percentage of production. However, their rate has decreased from 24.4% in 1940 to 21.5% in 1940, and to only 15.7% in 1953.

Fluctuations in the energy requirements of wood and paper industries have resulted mostly from the availability of secondary power for the processing of steam needed by these industries. However, the requirements of primary power has been on the upgrade since the end of the war when newsprint production in Canada amounted to some 3,600,000 tons, as against 5,721,000 tons in 1953.

The greatest increase in electricity requirements in Quebec was for the smelting and refining of Al. The electricity requirements of this industry which amounted to 2.5 billion kwhr in 1940 rose to 7.2 billion kwhr in 1948 and to 11.1 billion kwhr in 1953.

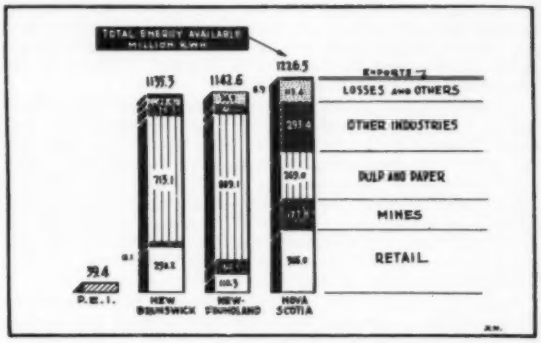

Fig. 7. Pattern of utilization of electricity in the Atlantic Provinces. The pattern of utilization of electricity in the Atlantic provinces differs considerably from that in the province of Quebec, as can be observed from the above chart which shows the 1953 utilization, in each one of the four provinces concerned.

At 39.4 million kwhr, the utilization of electricity in Prince Edward Island represents only about 365 kwhr per capita. Domestic service and commercial lighting account for 61% of the total utilization. In New Brunswick, utilization of electricity amounts to about 2,040 kwhr per capita. The largest portion (63%) is used in the pulp and paper industries, whereas other industries use only 6.5% and retail users about 22%. In Newfoundland, the pulp and paper industry absorbs 78% of the energy, retail services 9.5%, mines 5.2%, and other industries about 4.0%. The over-all utilization amounts to about 2,000 kwhr per capita. Utilization of electricity in Nova Scotia (1,850 kwhr per capita) is more diversified than in the other Atlantic provinces. Retail services use the greatest portion (30%), other industries use 24%, pulp and paper industry 22%, and mines about 14.5%.

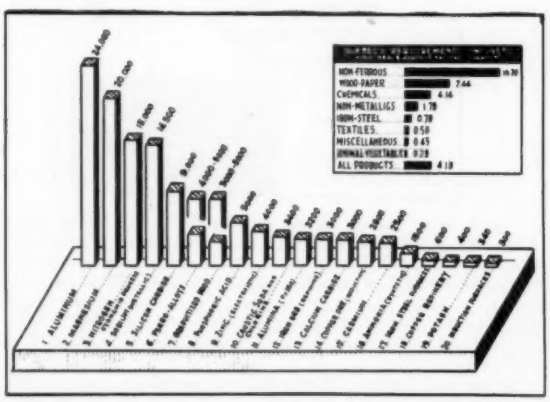

Fig. 8. Energy requirements of electrochemical and electrometallurgical industries. Of all electrometallurgical processes, the production of primary Al requires the largest volume of electricity. The 24,000 kwhr it uses per short ton of product compares with 20,000 kwhr for the production of metallic sodium, 4,000 for that of Zn, and about 3,000 kwhr for refining Fe and Cu ores.

Whereas the production of N by the cyanamid process requires 15,000 kwhr short ton of product, that of silicon carbide, an artificial abrasive second only to the diamond in scratch hardness, requires 9,000 kwhr.

Ferroalloys, produced in electric furnaces of the submerged arc type, require between 4,000 kwhr (in the case of the ferrosilicon with 15% silica) and 9,000 kwhr (for the ferromolybdenum with 75% molybdenum). Carbon and graphitized products are largely made in electric furnaces consuming between 3,000 and 8,000 kwhr ton of product. Phosphoric acid, derived from phosphate rock, is also an electrothermal product which requires about 5,000 kwhr/ton of contained phosphoric oxide.

Production of calcium carbide in electric furnaces of the submerged type requires about 3,000 kwhr/ton. Smelting of iron ore in electric furnaces is not commercially carried on in

the United States, but is practiced in Norway, Sweden, and Italy. Electric furnaces for melting iron and steel require some 340 kwhr/ton of metal.

In the province of Quebec, the industry which requires the largest quantity of electricity is the nonferrous metal group. The 16.20 kwhr it required in 1953 per thousand dollar worth of factory shipments was more than double the 7.44 kwhr required by the wood and paper group of industries and nearly four times the 4.14 kwhr required by the chemical group of industries. In comparison, nonmetallic industries need only 1.78 kwhr, iron and steel industries 0.78 kwhr, and the animal and vegetable group of industries only about 0.28 kwhr.

On the average, the industry in Quebec uses 49,500 kwhr per employee, or about 2.7 times as much as the industry in Ontario. In 1953, the smelting and refining of Al in Quebec absorbed about 1,000,000 kwhr per employee. In comparison pulp and paper mills used 322,000 kwhr and textile mills only about 13,000 kwhr.

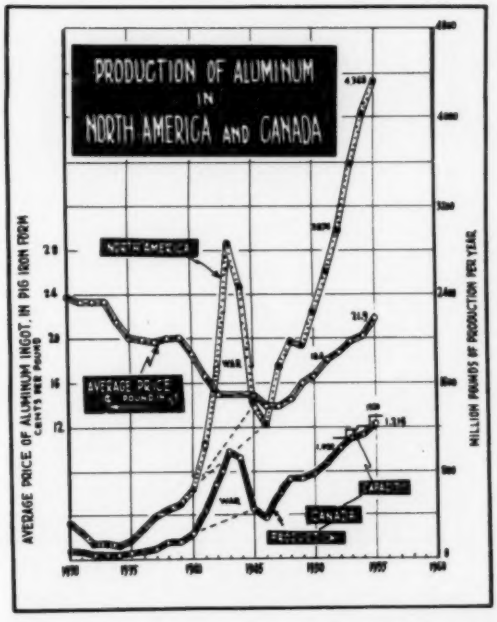

Fig. 9. Al production in North America. When, immediately after World War II, the production of Al in North America dropped from its war peak of about 2,800 million lb to about only 1,200 million lb, few people would have predicted that within six years that peak would be surpassed and that within nine years it would be exceeded by more than 50%. This is what has happened, and by the look of things the doubling of the war peak does not seem far removed, for already in 1955 the production is estimated to have attained 4,348 million lb.

Production of Al in Canada has also grown rapidly. From about 250 million lb in 1940 it quadrupled to 1,000 million lb at the peak of war activities in 1943. The postwar period saw the production drop to about 400 million lb in 1946. From that year on, the production rose rapidly to 800 million lb in 1950 and to 1,216 million lb in 1955.

Up to 1954, the Canadian production of Al came entirely from the Quebec plants of the Aluminum Co. of Canada, but in future the Kitimat plant of the same company will contribute an ever growing share until the top production of 550,000 tons a year will have been reached. By the end of 1956, the capacity of that plant will be around 181,000 tons and when the present $190 million program of expansion is completed in 1959, it will have reached 330,000 tons annually. By that time the total capacity of all Al plants in Canada is expected to have reached 912,000 tons.

Construction of a multimillion dollar Al plant by Canadian British Aluminium Limited in the Baie Comeau region will further increase the producing capacity of Quebec.

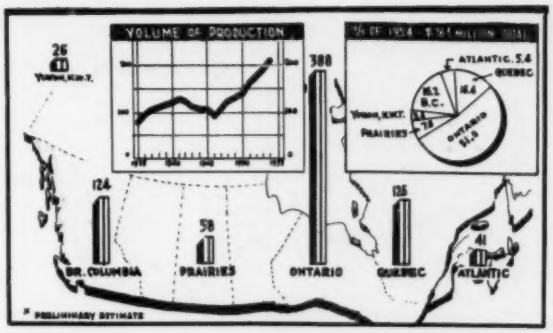

Fig. 10. Metallic mineral production of Canada. The value of the metallic mineral production of Canada in 1954 is shown by the Dominion Bureau of Statistics to have amounted to $763 million, of which 51.0% was produced in Ontario, 16.4% in Quebec, 16.2% in British Columbia, 7.6% in the Prairies, 5.4% in the Atlantic provinces, and 3.4% in the Yukon and Northwest Territories.

In 1954, the value of the metallic mineral production in Ontario, at $388 million, more than tripled the $126 million production of Quebec and the $124 million production of British Columbia. In comparison, the production in the Prairies amounted to only $58 million, that in the Atlantic provinces to $41, and that in the Yukon and Northwest Territories to $26 million. The volume of metallic mineral production of Canada in 1954 doubled those of 1935 and of 1946.

The exploitation in Quebec of the recently developed Fe ore resources, together with that of the Cu deposits in both Gaspe and Chibougamau districts, should considerably increase the value of the metallic mineral production in that province. The electrometallurgical industry in Quebec is bound to benefit from this development.

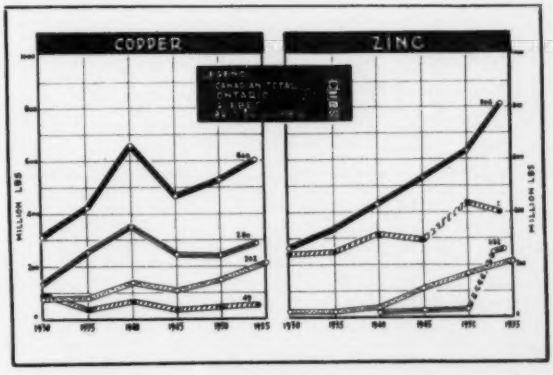

Fig. 11. Cu and Zn production in Canada. At 600 million lb, the Canadian production of Cu in 1954 was still about 50 million lb short of the peak 1940 production. In 1954, Ontario led the Canadian production with 280 million lb or 47% of the total, Quebec was second with 202 million lb, or about 33% of the total, and British Columbia followed with 49 million lb, or 8% of the total. Of the three provinces, Quebec was the only one in which the production exceeded that of 1940, it being about 70% higher.

Zn production in Canada, at 804 million lb, reached an all-time peak in 1954. The production in that year actually doubled the 1940 production and exceeded that of 1930 by 500 million lb.

Production of Zn in British Columbia has always been higher than in other parts of Canada. In 1930, the production already exceeded 200 million lb; between 1940 and 1945 it hovered around 300 million lb, and in 1950 it exceeded 400 million lb.

Since 1950, production of Zn in Ontario has increased from practically nothing to 282 million lb in 1954, when for the second consecutive year it exceeded that of Quebec. Up to 1940 the production of Zn in Quebec had never exceeded 30 million lb, but in 1945 it reached 112 million lb, in 1950, 172 million lb, and in 1954, 212 million lb.

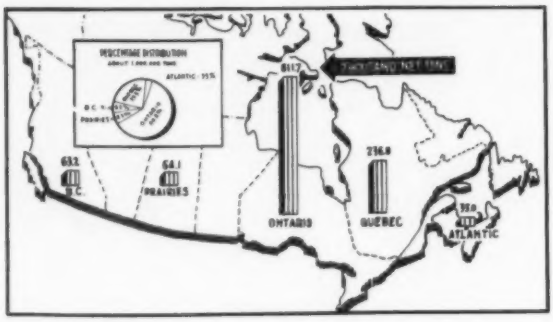

Fig. 12. Electric steel furnaces in Canada. The capacity of electric steel furnaces in Canada at the end of 1953 attained about one million tons and was distributed as indicated above. Ontario had about 61% of the total capacity, Quebec 24%, the Prairies and British Columbia each 6.4%, and the Atlantic provinces about 3.5%. Out of a total of 130 electric furnaces in Canada, Ontario had 75, Quebec 23, Nova Scotia 12, the Prairies 8, and British Columbia 12.

During the past 20 years the capacity has more than tripled from 309,885 tons in 1935, to 300,000 tons in 1940, 786,000 in 1945, 926,000 in 1950, and 987,675 tons in 1954. The 1953 production of electric steel in Canada amounted to 553,369 tons, including 487,509 tons of steel ingots and 75,360 tons of steel castings. The 1953 production was about 100,000 tons less than in 1952, but about 100,000 tons more than in 1944. During the period considered, production of electric steel, in relation to the total steel production, fluctuated as follows: 1944, 15.3%; 1950, 17.5%; and 1953, 13.4%.

New Address

for

The Electrochemical Society, Inc.

1860 Broadway New York 23, N. Y.

Telephones—CIrcle 5-6282, CIrcle 5-6283

The Electrochemical Society has moved its offices to new quarters, located on the northeast corner of 61st Street and Broadway. All communications to the Society and the JOURNAL should be addressed to the new address, 1860 Broadway.

Buffalo Program

THE ELECTROCHEMICAL SOCIETY

One Hundred and Twelfth Meeting

Sunday through Thursday

October 6, 7, 8, 9, and 10, 1957

CONDENSED TECHNICAL PROGRAM

Monday, October 7, 1957

Battery—(Abs. 1-10) 9:30 A.M.-12:00 M.; 2:00-5:00 P.M. (Maple Leaf Room)

Corrosion—Electrodeposition (Abs. 56-64) 9:45 A.M.-12:20 P.M.; 2:00-5:15 P.M. (Los Angeles Room)

Electronics—Semiconductors 9:30 A.M.-12:00 M.; 2:00-5:00 P.M. (Ballroom)

Electro-Organic (Abs. 79-85) 10:00 A.M.-12:00 M.; 2:00-3:30 P.M.; 3:30-5:00 P.M. Round Table (Empire State Room)

Electrothermics and Metallurgy (Abs. 98-100) 2:00-3:30 P.M. (New York Room)

Tuesday, October 8, 1957

Battery (Abs. 11-22) 9:00 A.M.-12:00 M.; 2:00-5:00 P.M. (Maple Leaf Room)

Corrosion (Abs. 29-39) 9:00-11:45 A.M.; 2:00-5:00 P.M. (Sheraton Hotel)

Electrodeposition (Abs. 65-73) 9:30 A.M.-12:00 M.; 2:00-4:00 P.M. (Buffalo Room)

Electronics—Semiconductors 9:30 A.M.-12:00 M.; 2:00-5:00 P.M. (Ballroom)

Electro-Organic (Abs. 86-95) 9:00-11:30 A.M.; 2:00-4:30 P.M. (Los Angeles Room)

Electrothermics and Metallurgy (Abs. 101-104) 9:15-11:45 A.M. (Georgian Room)

Wednesday, October 9, 1957

Battery (Abs. 23-28) 9:00 A.M.-12:00 M. (Maple Leaf Room)

Corrosion (Abs. 40-44) 9:00-11:30 A.M. (Georgian Room)

Electrodeposition (Abs. 74-78) 9:00 A.M.-12:15 P.M. (Buffalo Room)

Electronics—Semiconductors 9:30 A.M.-12:00 M. (Ballroom)

Electrothermics and Metallurgy (Abs. 105-108) 9:30-11:30 A.M. (Empire State Room)

Thursday, October 10, 1957

Battery 9:00 A.M.-12:00 M. Round Table (Ballroom)

Corrosion (Abs. 45-55) 9:00-11:45 A.M.; 2:00-5:00 P.M. (Georgian Room)

Electro-Organic (Abs. 96-97) 9:00-10:00 A.M.; 10:00 A.M.-12:00 M. Round Table (Empire State Room)

GENERAL INFORMATION

Convention Headquarters will be at the Hotel Statler, Delaware Ave. at Niagara Square, Buffalo, N. Y.

Rates per day for rooms (with bath) will be: single room $6.00 through $16.00; suites for one or two $24.00 through $37.00.

Requests for room reservations at the Headquarters Hotel should be mailed to the Front Office Manager, Hotel Statler, Delaware Ave. at Niagara Square, Buffalo 5, N. Y. *Be sure* to state your intention to attend The Electrochemical Society meeting.

Other hotels within a few blocks of the Headquarters Hotel and their minimum rates are:

Lafayette, Washington & Clinton Sts.,—single $5.00; double $9.00; twin-bed $10.00; suite $22.00.

Buffalo Hotel, Washington & Swan Sts.,—single $6.50 through $7.00; double-bed room $9.50 through $10.00; twin-bed room $11.00 through $12.00; suites for one or two $17.00 and $21.00. A suite for three persons is available at $27.00.

Sheraton Hotel, 75 Delaware Ave. —single $6.85 through $10.50; double-bed $9.35; twin-bed $10.35 through $14.00; suite $16.00 through $30.70; (free parking area).

Stuyvesant Hotel, 245 Elmwood Ave.—single $7.00 through $12.00; double-bed $10.00 through $14.00; twin-bed $13.00 through $20.00; suite $18.00 through $30.00; (free parking area).

There are numerous motels in or near Buffalo, but considerably farther from the Convention Headquarters. Three of these are as follows:

Mohawk Manor, 1640 Main St. (From the west, Route 20, from east or west, Route 3)—single $6.50 through $7.50; double-bed $10.00; twin-bed $10.50 through $12.50.

Towne House, 24 High St. at Main (Route 5)—single $7.00, $8.00, and $9.00; twin-bed $12.00, $14.00, and $16.00; at least two persons may be accommodated in each room of the Towne House, as each and every room has double beds.

Kenton Manor, 2075 Sheridan Dr. (Route 324)—single $7.00; double-bed $8.50; twin-bed $9.50; also room with a single and double-bed $10.50 or room with two double beds to accommodate possible four persons $12.50 and $16.00.

Accommodations may also be had at the local Y.M.C.A.

Requests for room reservations should include mention of The Electrochemical Society.

The Office of the Secretary will be in the Hartford Room on the Mezzanine Floor.

All technical sessions will be held on the Mezzanine Floor; the Tuesday sessions and luncheon of the Corrosion Division will be held at the Sheraton Hotel, 715 Delaware Ave., a 15-minute walk from the Hotel Statler.

Ladies' Headquarters will be in the Detroit Room on the Mezzanine Floor. For details, *see* Ladies' Program.

REGISTRATION

The registration desk will be in the lounge on the Mezzanine Floor. Following is the registration schedule:

Sunday, Oct. 6—3:00 P.M. to 9:00 P.M.

Monday, Oct. 7—8:00 A.M. to 5:00 P.M.

Tuesday, Oct. 8—8:30 A.M. to 5:00 P.M.

Wednesday, Oct. 9—8:30 A.M. to 5:00 P.M.

Thursday, Oct. 10—8:30 A.M. to 12:00 M.

Registration fees are:

Members	$ 7.00
Ladies	5.00
Nonmembers	13.00
Nonmembers (one day only)	5.00
Students	2.00

INFORMATION ABOUT BUFFALO AND NIAGARA FALLS

Buffalo, in the heart of the world-famous Niagara Region and at the gateway to Canada, is the hub of a great concentration of industrial and commercial activity. One of America's great inland water ports, Buffalo is now rapidly preparing for the opening of the St. Lawrence Seaway in 1959 which will make it a world port. The largest grain milling and distribution center in the world, Buffalo stands astride the busy terminals of 11 major railroads, and at the western terminus of the State Barge Canal and the New York State Thruway. It is the shipping or exchange point for the huge flow of traffic between East and West and to and from Canada.

Buffalo is the second largest city in New York State in population, second only to New York City, and the 15th in size in the nation. As of January 1, 1957 the population was 604,000, and total population in the Buffalo-Niagara Metropolitan area now stands at 1,223,000.

There is a great diversity of industry—both large and small manufacturers—in the Metropolitan Buffalo area. Among the leading industries are: steel works and rolling mills, chemicals, petroleum products, machinery, feed, flour, grain milling, rubber and nonferrous metal products, clothing, plastics, drugs, and furniture.

The University of Buffalo, with a total enrollment of approximately 11,000 in the student body, embraces a wide spectrum of education including Arts and Sciences, Business Administration, Chronic Disease Institute, Dentistry, General and Technical Studies, Engineering, Education, Graduate Arts and Sciences,

Law, Medical, Millard Fillmore College (night school), Nursing, Pharmacy, and Social Work. The Chancellor is Dr. Clifford C. Furnas.

Buffalo is also a city abounding in recreational and cultural values and beauty. It has a $3,000,000 zoo and 10 public parks containing over 3,000 acres of land. The fine traditions of American culture are expressed by Buffalo's Historical Museum, The Museum of Natural Sciences, The Albright Art Gallery, and other centers. The Albright Art Gallery is well known in international art circles for its collection of old masters and modern paintings and sculptures. Kleinhans Music Hall is another point of interest in Buffalo, and is the home of the renowned Buffalo Philharmonic Orchestra.

The Statler-Hilton Hotel is located on historic Niagara Square in the heart of the downtown area, and most convenient to business, shopping, and theatrical districts.

For those planning to participate in the "Niagara Falls Day" activities on Wednesday, there is a real treat in store. Niagara Falls is 25 miles north of Buffalo. In addition to its world renowned scenic splendor, it is also the center of one of the largest electrochemical and electrometallurgical production areas in the world. Some of the more important products are: chlorine, caustic soda and caustic potash, ferroalloys, carbon and graphite products, abrasives, resins and chlorinated organics, metallic sodium, paper and paper products, and lumber and millwork. Bell Aircraft's rocket and guided missiles plant is also situated here. Niagara University is located at Niagara Falls.

Climaxing "Niagara Falls Day" will be a cocktail and dinner party in the beautiful Rainbow Room of the Sheraton-Brock Hotel in Niagara Falls, Canada.

SYMPOSIA AND ROUND TABLES

The Battery Division has scheduled symposia on: Lead Oxides—Their Composition, Structure, and Importance in Storage Batteries; Importance of Design Factors on Storage Battery Performance; Unconventional Electrochemical Systems for Batteries; and a Round-Table Discussion of Fuel Cells.

The Corrosion Division and **Electrodeposition Division** have scheduled a joint symposium on Corrosion of Electrodeposited Metals.

The Electrodeposition Division has scheduled symposia on: Growth of Electrodeposits; and Electrolytic Metal Powders.

The Electronics Division—Semiconductor Group has scheduled symposia on: Elemental Semiconductors; Semiconductor Compounds and Alloys; Surface Phenomenon; Diffusion and Process Technology.

The Electro-Organic Division has scheduled symposia on: Arc Electrolysis; Cathodic Reduction of Organic Compounds; Polarography; a Round-Table Discussion on the Industrial Future of Electro-Organic Chemistry; a second Round-Table Discussion on the Application of Polarographic Techniques in the Pharmaceutical Field.

The Electrothermics and Metallurgy Division has scheduled a symposium on Ferroalloys and Slags.

GENERAL FUNCTIONS

Symposia Chairmen Breakfasts

On **Monday, Tuesday, Wednesday,** and **Thursday, October** 7, 8, 9, and 10, at 7:45 A.M., special breakfasts for all symposia chairmen will be held, on Monday and Wednesday in the St. Louis Room, on Tuesday in the Club Room, and on Thursday in the Detroit Room.

Monday Evening

Although no Society events are scheduled, the local committee will be glad to provide information regarding available dining and entertainment in Buffalo and assist in obtaining reservations and transportation.

Tuesday Palladium Medal Banquet

A reception and dinner in honor of the Palladium Medalist, the late Karl Friedrich Bonhoeffer, will be held at 6:30 P.M. in the Foyer of the Ballroom, Lobby floor. Dr. Bonhoeffer was head of the Max Planck Institute for Physical Chemistry. Cocktails will be served from 6:30 to 7:30 P.M. followed by dinner at 7:30 P.M. in the Ballroom.

Wednesday Evening Supper at Niagara Falls, Ontario

On Wednesday, October 9, an informal party will be held in the Rainbow Salon of the Sheraton Brock Hotel, Niagara Falls, Ont. The Rainbow Salon is located on the 10th floor of the hotel, and overlooks the Falls of Niagara. Cocktails will be served from 6:00 to 7:00 P.M.; a buffet supper will be served at 7:00 P.M. Illumination of the falls is scheduled for 8:30 P.M. Daylight Saving Time. Busses will depart at 9:30 P.M. for the return trip to Buffalo.

All plant visits in the Niagara Falls area are scheduled for Wednesday afternoon, and all these trips will converge at the Sheraton Brock Hotel in time for the party. The Ladies Scenic Tour of Niagara is also scheduled for Wednesday, and this trip will arrive at the Sheraton Brock in time for the party. For the convenience of members and guests who wish to attend the party at the Sheraton Brock and who are unable to leave sooner, a shuttle bus will leave the Delaware Ave. entrance of the Statler Hotel, Buffalo, at 5:00 P.M.

For the return trip to Buffalo, all busses will leave the Sheraton Brock promptly at 9:30 P.M., and the estimated time of arrival at the Hotel Statler is 10:30 P.M.

Tickets for the Brock Party and for transportation must be purchased at time of registration.

IMPORTANT: The Sheraton Brock Hotel is in *Canada*. Citizens of countries other than the U. S. and Canada should carry their passports and their visas for return entry to the United States. The U. S. Immigration Office advises that for naturalized citizens the law does not require that they carry their papers, but it is preferable since it simplifies and expedites crossings.

PLANT AND LABORATORY TOURS

Because of the number of trips which have been arranged for this meeting, registrants should purchase tickets early to insure that they can go on the trips of their choice. The maximum number for each tour is 90 persons. On trips into Canada, citizens of countries other than the United States and Canada must have passports or other means to insure re-entry into the United States. All busses leave from the Delaware Avenue entrance of the Hotel Statler.

Tuesday, October 8, 1:30 P. M.

Choice of two tours:

Trip No. 1—Cornell Aeronautical Laboratory, Inc., Buffalo, New York. —Trip limited to United States citizens. This laboratory, now administered by Cornell University, is the former research laboratory of Curtiss Wright Corp. It engages in contract research for the Air Force and others, particularly on aeronautical subjects. Visitors will be shown the big wind tunnel and also the supersonic and hypersonic tunnels and control rooms for these; also the high altitude chamber, the model shop, the flutter-study model plane, and other nonclassified areas. Collision impact safety studies will be illustrated in motion pictures. Laboratory personnel will explain various angles. Estimated time of return to hotel is 4:15 P.M. Bus fare $1.00. Chartered busses will leave the Delaware Ave. entrance of the Hotel Statler at 1:30 P.M.

Trip No. 2—Carborundum Metals Division of the Carborundum Co., Akron, N. Y. (20 miles east of Buffalo)—This modern plant is the pioneering commercial producer of zirconium and hafnium metals in sponge and ingot form of high purity suitable for nuclear reactor and corrosion-resisting uses. Visitors will see the entire process (recently declassified), starting with crude zirconium chloride which is dissolved, put through a liquid-liquid extraction process to separate hafnium from the zirconium, and then reconverted to chloride which is reduced to sponge in a modified Kroll process. Ingot melting facilities will also be shown, together with the modern research, control, and spectrographic laboratories. Chartered busses will leave the Delaware Ave. entrance of the Hotel Statler at 1:30 P.M. Bus fare $1.50. Estimated time of return to the hotel is 5:00 P.M.

Wednesday, October 9, 1:30 P. M. (Niagara Falls Day)

Choice of three simultaneous tours, each of which will terminate at the Sheraton Brock Hotel in Niagara Falls, Ontario, at approximately 5:30 P.M. for cocktails and dinner, followed by return to Buffalo past the illuminated falls and along the Canadian shore, re-entering United States via the Peace Bridge at Buffalo. Chartered busses will leave the Delaware Ave. entrance of the Hotel Statler promptly at 1:30 P.M. Bus fare for each tour is $2.50.

Trip No. 3—International Nickel Co., Port Colborne, Ont.—Visit limited to United States or Canadian

citizens. This plant receives crushed sulfide concentrates from the mines in Northern Ontario. Visitors will see these fired in reverberatory furnaces, anode forming, and refining operations conducted in the largest electroplating room in the world, covering some 12 acres. Both nickel and cobalt are produced in the form of sheet and shot. Black and green oxides are also produced for the ceramic trade and for the manufacture of ferrites for the electronics industry. Chlorination and other chemical processing steps of interest are involved.

Trip No. 4—Metals Research Laboratories, Electro Metallurgical Co. and Hooker Electrochemical Co., Niagara Falls, N. Y.—The Niagara Falls Metals Research Laboratories handle all metallurgical research for the Union Carbide Corp., including Electro Metallurgical Co. and Haynes Stellite Co. Divisions.

This modern, newly expanded laboratory entirely devoted to metallurgical research is one of the most comprehensive laboratories of this type in the United States. Complete facilities are available for development of metals and alloys, including furnaces, forging hammers, rolling mills, x-ray diffraction, metallographic equipment, physical testing, welding, and chemical processing equipment.

The group will then be taken to the chlorine-caustic soda plant of Hooker Electrochemical Co., where they will visit the cell rooms with Hooker Type S and Type S-3A cells, chlorine liquefication and caustic soda evaporation. This is the home plant of the Hooker Type cell which is used in 40 plants in the United States and other countries.

Trip No. 5—North American Cyanamid, Ltd., Niagara Falls, Ont., and Ontario Hydro Power Plant, Queenston, Ont.—Open to all. Our party will cross into Canada on the Peace Bridge and drive along the scenic Niagara River to the North American Cyanamid plant. Here they will see the preparation of raw materials (lime and coke) followed by furnacing in 21,000 kw furnaces to form calcium carbide, then the crushing and milling of the carbide and its nitrification to form cyanamid, and finally the milling of this into finished product. A large liquid air plant furnishes the nitrogen for the process. This is the 50th Anniversary of the company on its present site.

Next the group will be taken to the new Sir Adam Beck Generating Station No. 2 of the Ontario Hydro Commission, opened August 30, 1954, with a capacity of 1,828,000 hp at a cost of nearly $344,000,000. Just beyond is Sir Adam Beck Station No. 1 opened December 29, 1921.

Water for the new station enters two intake structures 2 miles above the Falls, passing through twin 5½ mile tunnels, diving 330 ft under the City of Niagara Falls and entering a 2½ mile open cut canal. The tunnels have a diameter of 45 ft and their construction required removal of over 4 million cubic yards of rock. In building the canal and forebay, more than 8 million cubic yards of rock were removed.

LADIES PROGRAM

Ladies' Headquarters will be in the Club Room on Sunday, Detroit Room on Monday, Tuesday, and Wednesday, and in the Boston Room on Thursday. A member of the Ladies' Committee will be in the Ladies' Headquarters on Sunday from 3:00 to 9:00 P.M. to welcome and assist the ladies in every way.

The temperature in Buffalo during early October is usually in the 50°-70° range. Buffalo is a windy city.

Monday morning, October 7—A get-together period with coffee will be held in the Ladies' Headquarters (Detroit Room) starting at 9:30 A.M. (complimentary).

Monday afternoon, October 7—A complimentary luncheon will be given at the Park Lane Hotel starting at 1:00 P.M. After the luncheon, the ladies will hear a talk by a member of the Jane Keeler Studio Theatre Group. The ladies will leave from the Delaware Ave entrance of the Hotel Statler at 12:30 P.M. and will return about 3:00 P.M. The remainder of the afternoon will be open for shopping or individual sight-seeing. (Tickets complimentary).

Monday evening, October 7—Although no Society events are scheduled, the Local Committee will be glad to provide information about available dining and entertainment in Buffalo and assist in obtaining reservations and transportation.

Tuesday morning and afternoon, October 8—Coffee will be served in Ladies Headquarters (Detroit Room) at 9:30 A.M. (complimentary). The ladies are invited to luncheon and bridge at the beautiful Buffalo Country Club on the Onondaga Escarpment (with the compliments of the Buffalo Electrochemical Co., Division of Food Machinery Corp.). For ladies not interested in bridge, the Committee will provide transportation after lunch to other places of interest. Chartered bus will be boarded at the Delaware Ave entrance of the Hotel Statler at 12.00 M. The bus will return to the hotel about 4:00 P.M. (tickets complimentary).

Tuesday evening, October 8—The ladies are invited to attend the Palladium Medal Reception and Banquet at 6:30 P.M. (tickets should be purchased at time of registration.)

Wednesday morning, afternoon, and evening, October 9—Niagara Falls Day—Coffee will be served in Ladies' Headquarters (Detroit Room) at 9:30 A.M. (complimentary).

At 11:00 A.M. ladies will meet at the Delaware Ave. entrance of the Hotel Statler, to board the bus for a tour of the Niagara Frontier. Luncheon will be served enroute at the Niagara Falls Country Club at 1:15 P.M. In the afternoon, historic Old Fort Niagara, at the mouth of the Niagara River, will be visited. The party will then cross into Canada passing through Queenston and Victoria Parks. The ladies will then join the members at the Hotel Sheraton Brock, at Niagara Falls, Ont., where cocktails and a buffet supper will be served in the Rainbow Salon; busses will leave the Sheraton Brock promptly at 9:30 P.M. and the return trip will be made along the Canadian side of the river and over the Peace Bridge. Estimated time of arrival at the Statler Hotel is 10:30 P.M. (tickets for this trip should be purchased at time of registration.)

IMPORTANT—Citizens of countries *other than* the United States and Canada must carry passports and visas.

For *naturalized* citizens, the Immigration Office advises that the law does not require evidence of naturalization, but that having Naturalization Papers is preferable in that it simplifies and expedites crossing.

Thursday morning, October 10—Coffee will be served at 9:30 A.M. in the Ladies' Headquarters (Boston Room) (complimentary). This morning and afternoon have been left open for shopping and informal tours. The Hotel Statler is within walking distance of the shopping and theater districts.

LUNCHEONS AND BUSINESS MEETINGS OF DIVISIONS

Battery Division Luncheon and Business Meeting, Tuesday, October 8, at 12:30 P. M. in the Maple Leaf Room.

Corrosion Division Luncheon and Business Meeting, Tuesday, October 8, at 12:30 P. M. at the Sheraton Hotel, 715 Delaware Ave., a 15-minute walk from the Hotel Statler.

Electrodeposition Division Business Meeting, Tuesday, October 8, at 4:00 P. M. in the Buffalo Room.

Electro-Organic Division Luncheon and Business Meeting, Monday, October 7, at 12:30 P. M. in the New York Room.

MEETING ROOM SCHEDULES

Meeting	Monday		Tuesday		Wednesday		Thursday	
	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.
Battery	A	A	A	A	A		B	
Corrosion			C	C	D		D	D
Corrosion—Electrodeposition	E	E						
Electrodeposition			F	F	F			
Electronics—Semiconductors	B	B	B	B	B			
Electro-Organic	G	G	E	E			G	
Electrothermics and Metallurgy		H	D		G			

A = Maple Leaf Room
B = Ballroom
C = Sheraton Hotel, 715 Delaware Ave.
D = Georgian Room
E = Los Angeles Room
F = Buffalo Room
G = Empire State Room
H = New York Room

BOARD AND COMMITTEE MEETINGS

Sunday, October 6, 2:00 P. M.—Meeting of the Board of Directors in the St. Louis Room.

Monday, October 7, 5:00 P. M.—Meeting of the Council of Local Sections in the Grover Cleveland Room.

Monday, October 7, 5:00 P. M.—Meeting of the Editorial Staff of the JOURNAL in the Hartford Room.

Tuesday, October 8, 5:00 P. M.—Meeting of the Membership Committee in the Grover Cleveland Room.

Thursday, October 10, 12:00 M.—Meeting of General Chairmen of Future Meetings in the Hartford Room.

COST OF VARIOUS FUNCTIONS

(other than registration)

Symposia Chairmen Breakfasts	$2.50
Division Luncheons	3.00
Tuesday Reception and Banquet	
Gentlemen	7.00
Ladies	4.00
Wednesday Evening Party at Sheraton-Brock	
Gentlemen	5.50
Ladies	4.00
Trip No. 1 to Cornell Aeronautical Laboratory (transportation)	1.00
Trip No. 2 to Carborundum Metals (transportation)	1.50
Trip No. 3 to International Nickel (transportation)	2.50
Trip No. 4 to Metals Research Lab and Hooker Electrochemical (transportation)	2.50
Trip No. 5 to North American Cyanamid and Sir Adam Beck Power Station (transportation)	2.50
Trip No. 6 direct to Sheraton-Brock Hotel (transportation only)	1.75
Ladies' Functions:	
Trip No. L-1 to Park Lane, luncheon and transportation, complimentary	
Trip No. L-2 to Buffalo Country Club, Luncheon and Transportation, complimentary	
Trip No. L-3 all-day tour of Niagara Frontier (including luncheon at the Niagara Falls Country Club, but not including tickets for dinner at the Sheraton-Brock)	4.00

JOURNALS

Copies of the July, August, September, and October issues of the JOURNAL of The Electrochemical Society will be available at the registration desk. The price of a single copy of the JOURNAL is $1.25 to members and $1.75 to nonmembers.

EXTENDED ABSTRACTS

The Battery Division is making available an extended abstract booklet containing 1000-word abstracts of most of the papers presented at the Division's Buffalo symposia. Copies of the booklet will be on sale for $2.00 at the registration desk.

DISCUSSION

No recordings will be made of oral discussions. Those contributing to the discussion of a paper and desiring their remarks to be published will be supplied by the symposium chairman with a printed form on which any discussion may be written. These forms should be given to the Secretary-Treasurer of the Division or to the Managing Editor of the JOURNAL after the session; they can be mailed to the Managing Editor of the JOURNAL, 1860 Broadway, New York 23, N. Y. The discussion will then be referred to the author for reply. Publication of the discussion and the comments of the author depends on publication of the article in the JOURNAL.

Written discussion should be submitted within two months following publication of the article in the JOURNAL. A Discussion Section is published semiannually in the JOURNAL.

EMPLOYMENT POSTERS

Companies which desire to recruit employees at the Buffalo Meeting will have posters to this effect on a bulletin board near the registration desk.

Technical Program

Monday, October 7, 1957

9:00 A.M.—Formal Opening of the 112th Meeting with Introduction by General Chairman Robert B. MacMullin and Response by President Norman Hackerman (Ballroom).

NOTE

In the Index to Authors, the abstract number is used. Address of author(s) is included with the abstract.

BATTERY

Monday, October 7, 1957

Lead Oxides—Their Composition, Structure, and Importance in Storage Batteries
with E. Willihnganz presiding
(MAPLE LEAF ROOM)

9:30 A.M.—"The Anodic Oxides on Lead" by Jeanne Burbank (Abstract No. 1)

10:10 A.M.—"The Electrochemical Properties of the PbO_2 and the Anodic Corrosion of Lead and Lead Alloys" by Paul Ruetschi (Abstract No. 2)

10:50 A.M.—"The Correction of X-Ray Diffraction Powder Photographs for Highly Absorbing Samples" by P. E. Jensen and E. J. Ritchie (Abstract No. 3)

11:30 A.M.—"The Unit Cell of Yellow Litharge" by P. E. Jensen and E. J. Ritchie (Abstract No. 4)

Battery (cont'd)

Monday, October 7, 1957

Importance of Design Factors on Storage Battery Performance
with E. J. Ritchie presiding
(MAPLE LEAF ROOM)

2:00 P.M.—"Changes in Positive Active Material Density during Various Conditions of Service" by J. F. Dittmann and J. F. Sams (Abstract No. 5)

2:30 P.M.—"The Action of Silver and Cobalt at the Positive Plate of the Lead-Acid Battery" by J. J. Lander (Abstract No. 6)

3:00 P.M.—"Influence of Positive Grid Alloy and Element Design on Battery Performance" by H. Stoertz (Abstract No. 7)

3:30 P.M.—"Design and Quality Control in the Battery Industry through Microscopy" by A. C. Simon and E. L. Jones (Abstract No. 8)

4:00 P.M.—"Designing for Quality" by H. J. Strauss (Abstract No. 9)

4:30 P.M.—"Design Factors for Nickel-Cadmium Batteries" by Arthur Fleischer, R. E. Rockey, and G. B. Ellis (Abstract No. 10)

Battery (cont'd)

Tuesday, October 8, 1957

General Session
with W. S. Herbert presiding
(MAPLE LEAF ROOM)

9:00 A.M.—"Improvement in Negative Plate Performance" by Arthur Fleischer (Abstract No. 11)

9:30 A.M.—"Cinemicrography of the Freezing Process in Lead-Antimony Grid Alloys" by A. C. Simon and E. L. Jones (Abstract No. 12)

10:00 A.M.—"Measurement of the Internal Resistance of Standard Cells" by G. D. Vincent (Abstract No. 13)

10:30 A.M.—"A New Approach to Resistance Measurements of Dry Cells" by R. J. Brodd (Abstract No. 14)

11:00 A.M.—"Formation of Manganese (II) Ion in the Discharge of the Manganese Dioxide Electrode, II. Effect of Volume and pH of Electrolyte" by W. C. Vosburgh, M. J. Pribble, Akiya Kozawa, and Ahmed Sam (Abstract No. 15)

11:30 A.M.—"The Relation of the Conditions of Electrodeposition of Manganese Dioxide to the Discharge Characteristics" by Akiya Kozawa and W. C. Vosburgh (Abstract No. 16)

12:30 P.M.—Battery Division Luncheon in the Maple Leaf Room.

Battery (cont'd)

Tuesday, October 8, 1957

Unconventional Electrochemical Systems for Batteries
with C. K. Morehouse presiding
(MAPLE LEAF ROOM)

2:00 P.M.—"Studies of the Vapor Pressure and the Density of Electrolytes for Dry Cells" by Kumazo Sasaki (Abstract No. 17)

2:30 P.M.—"A Magnesium Sea-Water Battery" by J. J. Shotwell and R. C. Kirk (Abstract No. 18)

3:00 P.M.—"Ammonia Vapor-Activated Reserve Batteries" by H. S. Gleason, J. M. Freund, L. J. Minnick, and W. F. Meyers (Abstract No. 19)

3:30 P.M.—"A Unique Dry Battery" by H. B. Reed, Jr., and M. B. Goldberg (Abstract No. 20)

4:00 P.M.—"Indium as an Anode Material" by T. L. Boswell (Abstract No. 21)

4:30 P.M.—"Halogen-Activated Solid Electrolyte Cell" by J. L. Weininger (Abstract No. 22)

Battery (cont'd)

Wednesday, October 9, 1957

Unconventional Electrochemical Systems for Batteries
Organic Cathodes
with U. B. Thomas presiding
(MAPLE LEAF ROOM)

9:00 A.M.—"An Investigation of Some New Cathode Depolarizer Materials" by A. B. Tripler, Jr., and L. D. McGraw (Abstract No. 23)

9:30 A.M.—"Investigations of Electrochemical Characteristics of Organic Compounds, I. Aromatic Nitro Compounds" by R. Glicksman and C. K. Morehouse (Abstract No. 24)

10:00 A.M.—"Nitro Aromatic-Magnesium Dry Cells" by C. K. Morehouse and R. Glicksman (Abstract No. 25)

10:30 A.M.—"Investigations of Electrochemical Characteristics of Organic Compounds, II. Aromatic Nitroso Compounds" by R. Glicksman and C. K. Morehouse (Abstract No. 26)

11:00 A.M.—"Nitroso Aromatic-Magnesium Dry Cells" by C. K. Morehouse and R. Glicksman (Abstract No. 27)

11:30 A.M.—"N-Halogen Reserve Batteries" by G. S. Lozier, L. H. Cutler, and C. K. Morehouse (Abstract No. 28)

Battery (cont'd)

Thursday, October 10, 1957

Round-Table Discussion of Fuel Cells with G. W. Heise presiding

(BALLROOM)

9:00 A.M.-12:00 M.—This discussion will be led by a number of panel members and will cover basic aspects of fuel cell electrochemistry, cells with aqueous electrolytes, cells with fused salt electrolytes, and fuel sources.

CORROSION

Tuesday, October 8, 1957

with C. V. King presiding

(SHERATON HOTEL)

9:00 A.M.—"The Germanium-Water-Oxygen System: Kinetics of the Dissolution Process" by W. W. Harvey and H. C. Gatos (Abstract No. 29)

9:30 A.M.—"Oxidation of Copper Single Crystals in Oxygen-Saturated Water at Room Temperature" by Jerome Kruger (Abstract No. 30)

10:15 A.M.—"Metal-Water Reactions, IV. Kinetics of the Reaction between Calcium and Water Vapor" by H. J. Svec and Charles Apel (Abstract No. 31)

10:45 A.M.—"Metal-Water Reactions, V. Kinetics of the Reaction between Magnesium and Water Vapor" by H. J. Svec and D. S. Gibbs (Abstract No. 32)

11:15 A.M.—"Electrochemical Polarization, III. Further Aspects of the Shape of Polarization Curves" by Milton Stern (Abstract No. 33)

12:30 P.M.—Corrosion Division Luncheon and Business Meeting at the Sheraton Hotel.

Corrosion (cont'd)

Tuesday, October 8, 1957

with C. V. King presiding

(SHERATON HOTEL)

2:00 P.M.—"Electrochemistry of Magnesium" by G. R. Hoey and M. Cohen (Abstract No. 34)

2:30 P.M.—"Use of High Purity Aluminum and Its Alloys in Controlling the Corrosion of Magnesium Alloys, I. The Galvanic Compatibility of Aluminum Alloys with Magnesium Alloys" by M. R. Bothwell (Abstract No. 35)

3:00 P.M.—"Use of High Purity Aluminum and Its Alloys in Controlling the Corrosion of Magnesium Alloys, II. The Protection of Magnesium Alloys by Aluminum" by M. R. Bothwell (Abstract No. 36)

3:30 P.M.—"Reaction of Aluminum and Carbon Tetrachloride, I." by J. D. Minford, M. H. Brown, and R. H. Brown (Abstract No. 37)

4:00 P.M.—"Reaction of Aluminum and Carbon Tetrachloride, II" by R. H. Brown, E. H. Cook, M. H. Brown, and J. D. Minford (Abstract No. 38)

4:30 P.M.—"Accelerated Corrosion in Aluminum-Silver Alloys" by H. H. Stadelmaier and E. M. Whitener (Abstract No. 39)

Corrosion (cont'd)

Wednesday, October 9, 1957

with M. A. Streicher presiding

(GEORGIAN ROOM)

9:00 A.M.—"Room Temperature Tarnishing of Silver in Bromine and Iodine" by J. L. Weininger (Abstract No. 40)

9:30 A.M.—"Effect of Steel, Passivating Solution, and Corrosive Media Variations on the Electrochemical Method of Detecting Hydrogen Diffusion through Steel" by T. J. Butler (Abstract No. 41)

10:00 A.M.—"Cathodic Reduction of Oxide Films on Iron, II. Determination of α-Fe_2O_3 and Fe_3O_4." by K. H. Buob, A. F. Beck, and M. Cohen (Abstract No. 42)

10:30 A.M.—"Chemical Factors Affecting Stress Corrosion Cracking of 18-8 Stainless Steels" by H. H. Uhlig and John Lincoln, Jr. (Abstract No. 43)

11:00 A.M.—"The Effect of Gamma Irradiation on the Potential Behavior of Platinum and Stainless Steel Electrodes" by W. E. Clark (Abstract No. 44)

Corrosion (cont'd)

Thursday, October 10, 1957

with J. E. Draley presiding

(GEORGIAN ROOM)

9:00 A.M.—"The Diffusion of Oxygen in Zirconium" by J. P. Pemsler (Abstract No. 45)

9:30 A.M.—"Formation Fields and Current Efficiencies in the Anodic Oxidation of Zirconium: A Direct Comparison of High Potential Formation Fields with Those Derived from Low Potential Charging Curves" by G. B. Adams, Jr., T. S. Lee, and Pierre Van Rysselberghe (Abstract No. 46)

10:15 A.M.—"The Reaction of Zirconium with Water Vapor at Subatmospheric Pressures" by M. W. Mallett, W. M. Albrecht, and R. E. Bennett (Abstract No. 47)

10:45 A.M.—"Reaction of Hydrogen with Preoxidized Zircaloy-2 at 300°-400°C" by E. A. Gulbransen and K. F. Andrew (Abstract No. 48)

11:15 A.M.—"The Effect of Pre-Oxidation in Oxygen on the Steam Corrosion Behavior of Zircaloy-2" by D. E. Thomas and S. Kass (Abstract No. 49)

Corrosion (cont'd)

Thursday, October 10, 1957

with J. E. Draley presiding

(GEORGIAN ROOM)

2:00 P.M.—"Electrolytic Etching of Dense Tantalum" by A. L. Jenny and R. A. Ruscetta (Abstract No. 50)

2:30 P.M.—"Metallographic Manifestations of the Air Oxidation of Tantalum at 750°C" by Robert Bakish (Abstract No. 51)

3:00 P.M.—"Nucleation of Crystalline Ta_2O_5 during Field Crystallization" by D. A. Vermilyea (Abstract No. 52)

3:30 P.M.—"Ionic Conductivity of Anodic Films at High Field Strengths: Transient Behavior" by D. A. Vermilyea (Abstract No. 53)

4:00 P.M.—"Annealing Anodic Ta_2O_5 Films: Changes in Dissolution Behavior and X-Ray Scattering" by D. A. Vermilyea (Abstract No. 54)

4:30 P.M.—"Effect of Ultraviolet Irradiation on the Growth of Anodic Ta_2O_5 Films" by D. A. Vermilyea (Abstract No. 55)

CORROSION—ELECTRODEPOSITION

Joint Symposium

Monday, October 7, 1957

Corrosion of Electrodeposited Metals with F. A. Lowenheim presiding

(LOS ANGELES ROOM)

9:45 A.M.—"The Mechanism of Corrosion of Copper-Nickel-Chromium Coatings" by H. J. Read (Abstract No. 56)

10:30 A.M.—"Double Nickel Coatings" by B. B. Knapp and R. J. McKay (Abstract No. 57)

11:10 A.M.—"Effects of Acoustical Waves on the Electrodeposition of Chromium" by Joseph Dereska, Ernest Yeager, and Frank Hovorka (Abstract No. 58)

11:50 A.M.—"Electrodeposition of Chromium Alloys—A Literature Review" by Charles Levy (Abstract No. 59)

Corrosion-Electrodeposition Joint Symposium (cont'd)

Monday, October 7, 1957

Corrosion of Electrodeposited Metals with H. R. Copson presiding

(LOS ANGELES ROOM)

2:00 P.M.—"The Protective Value of Tin-Nickel Alloy Deposits on Steel" by F. A. Lowenheim, W. W. Sellers, and F. X. Carlin (Abstract No. 60)

2:40 P.M.—"Electrodeposition of Manganese and Manganese Alloys: A Literature Survey" by E. L. MacNamara (Abstract No. 61)

3:20 P.M.—"Statistical Designs for Corrosion Testing" by W. Rowan (Abstract No. 62)

4:00 P.M.—"Comparison of Salt Spray Corrosion Rates for Tin Plated Copper in Different Locations" by M. S. Frant (Abstract No. 63)

4:40 P.M.—"The Performance of Supplementary Chromate Films

on Zinc" by F. R. Nagley, K. L. Procter, and H. L. Katz
(Abstract No. 64)

ELECTRODEPOSITION

Tuesday, October 8, 1957
Growth of Electrodeposits
with S. Barnartt presiding
(BUFFALO ROOM)

9:30 A.M.—"Filamentary Growths on Copper Cathodes" by T. C. J. Ovenston, C. A. Parker, and A. E. Robinson
(Abstract No. 65)

10:00 A.M.—"Microstructure of Copper Electrodeposited on Copper" by T. H. Orem
(Abstract No. 66)

10:30 A.M.—"Electron Microscope Studies on Copper Electrodes in Copper Plating Baths" by Shinzo Okada and Saburo Magari (Abstract No. 67)

11:00 A.M.—"The Structure of Electrodeposited Nickel" by B. C. Banerjee and A. Goswami
(Abstract No. 68)

11:30 A.M.—"Effect of Magnesium Sulfate on Nickel Plating Baths" by Ahmad Geneidy, W. A. Koehler, and Willi Machu
(Abstract No. 69)

Electrodeposition (cont'd)
Tuesday, October 8, 1957
with A. Brenner presiding
(BUFFALO ROOM)

2:00 P.M.—"Electroplating of Titanium and Other Polyvalent Metals from Molten Salt Electrolyte" by R. S. Dean, W. W. Gullett, and F. X. McCawley
(Abstract No. 70)

2:30 P.M.—"The Electrolytic Preparation of Titanium from Fused Salts, I. Preliminary Electrolytic Studies with Diaphragmed Cells" by M. B. Alpert, F. J. Schultz, and W. F. Sullivan (Abstract No. 71)

3:00 P.M.—"An Evaluation of Some Factors Involved in the Mechanical Testing of Electrodeposits" by T. J. Whalen and H. J. Read (Abstract No. 72)

3:30 P.M.—"Some Testing Cells for the Study of Electroplating Devices" by J. K. Shwirzynski and M. Huttly
(Abstract No. 73)

4:00 P.M.—Electrodeposition Division Business Meeting in the Buffalo Room.

Electrodeposition (cont'd)
Wednesday, October 9, 1957
Electrolytic Metal Powders
with C. A. Snavely presiding
(BUFFALO ROOM)

9:00 A.M.—"Electrolytic Metal Powders—Production and Applications" by K. H. Roll
(Abstract No. 74)

9:40 A.M.—"Electrodeposition of Powders for Powder Metallurgy" by C. L. Mantell
(Abstract No. 75)

10:20 A.M.—"Electrolytic Iron Powders—Production and Properties" by W. M. Shafer
(Abstract No. 76)

11:00 A.M.—"Electrolytic Iron Powder from a Caustic Bath" by Adrien Le Duc and Luther Vaaler (Abstract No. 77)

11:40 A.M.—"Electrolytic Copper Powder—Production and Properties" by E. J. Clugston and Frank Willis
(Abstract No. 78)

ELECTRONICS—SEMICONDUCTORS

Monday, October 7, 1957
Elemental Semiconductors
with P. H. Keck presiding
(BALLROOM)

9:30 A.M.-12:00 M.—A complete program including an abstract of each paper will be mailed to the Electronics Division-Semiconductor Group mailing list early in September. The program will also be available at the meeting.

Electronics—Semiconductors (cont'd)
Monday, October 7, 1957
Elemental Semiconductors
with S. Angello presiding
(BALLROOM)

2:00 P.M.-5:00 P.M.—A complete program including an abstract of each paper will be mailed to the Electronics Division-Semiconductor Group mailing list early in September. The program will also be available at the meeting.

Electronics—Semiconductors (cont'd)
Tuesday, October 8, 1957
Semiconductor Compounds and Alloys
with D. A. Jenny presiding
(BALLROOM)

9:30 A.M.-12:00 M—A complete program including an abstract of each paper will be mailed to the Electronics Division-Semiconductor Group mailing list early in September. The program will also be available at the meeting.

Electronics—Semiconductors (cont'd)
Tuesday, October 8, 1957
Surface Phenomenon
with E. N. Clark presiding
(BALLROOM)

2:00 P.M-5:00 P.M.—A complete program including an abstract of each paper will be mailed to the Electronics Division-Semiconductor Group mailing list early in September. The program will also be available at the meeting.

Electronics—Semiconductors (cont'd)
Wednesday, October 9, 1957
Diffusion and Process Technology
with M. Tanenbaum presiding
(BALLROOM)

9:30 A.M.-12:00 M.—A complete program including an abstract of each paper will be mailed to the Electronics Division-Semiconductor Group mailing list early in September. The program will also be available at the meeting.

ELECTRO-ORGANIC

Monday, October 7, 1957
Arc Electrolysis
with M. J. Allen presiding
(EMPIRE STATE ROOM)

10:00 A.M.—"Glow-Discharge Electrolysis in Aqueous Solutions" by A. R. Denaro and A. Hickling (Abstract No. 79)

Cathodic Reduction of Organic Compounds

10:30 A.M.—"Electrolytic Reduction of Cyanamide, II. Nature of the Reduction of Cyanamide and Formamidine" by Keijiro Odo, Eiichi Ichikawa, Katsujiro Shimogai, and Kiichiro Sugino
(Abstract No. 80)

11:00 A.M.—"Electrolytic Reduction of Organic Compounds, VII. Furfural" by D. D. Staker and and C. L. Wilson
(Abstract No. 81)

11:30 A.M.—"Electrolytic Reduction of Organic Compounds, VIII. Acetone" by G. W. Mansel and C. L. Wilson (Abstract No. 82)

12:30 P.M.—Electro-Organic Luncheon and Business Meeting in the New York Room.

Electro-Organic (cont'd)
Monday, October 7, 1957
Cathodic Reduction of Organic Compounds
with G. W. Thiessen presiding
(EMPIRE STATE ROOM)

2:00 P.M.—"An Electrolytic Study of the Course of the Clemmensen Reduction" by R. A. Strehlow and Sherlock Swann, Jr.
(Abstract No. 83)

2:30 P.M.—"Application of Electrodialysis to Halide Interconversion in Quaternary Salts" by M. J. Allen and J. Ocampo
(Abstract No. 84)

3:00 P.M.—"Electrochemical Reduction of the C_4 Dibasic Acids and Their Esters: Acetylenedicarboxylic, Dibromomaleic, and Dibromofumaric. Nature of the Products and Reaction Mechanisms" by P. J. Elving, Isadore Rosenthal, J. R. Hayes, and A. J. Martin (Abstract No. 85)

3:30 P.M.—Round-table discussion on the **Industrial Future of Electro-Organic Chemistry** with M. J. Allen, S. Swann, and C. L. Wilson.

Electro-Organic (cont'd)
Tuesday, October 8, 1957
Polarography
with S. Wawzonek presiding
(LOS ANGELES ROOM)

9:00 A.M.—"Solid Electrode Voltammetry of Organic Compounds" by Theodore Kuwana, T. R. Mueller, and R. N. Adams
(Abstract No. 86)

9:30 A.M.—"Electrochemical Studies in Cyclic Carbonate Esters" by C. W. Tobias
(Abstract No. 87)

10:00 A.M.—"Polarographic Studies in Dimethylformamide, IV. Behavior of Aldehydes and Ketones" by S. Wawzonek and A. A. Gundersen
(Abstract No. 88)

10:30 A.M.—"Polarographic Reduction of Some Acetylenic Linkages" by A. H. Gropp and J. C. Ramsey, Jr. (Abstract No. 89)

11:00 A.M.—"Polarographic Reduction of Some Nitrofluorenones" by Julia Gary, R. M. Powers, and R. A. Day, Jr. (Abstract No. 90)

Electro-Organic (cont'd)
Tuesday, October 8, 1957
Polarography
with P. J. Elving presiding
(LOS ANGELES ROOM)

2:00 P.M.—"Electrochemical Reduction of Some Nitramines and Nitrosamines, I. Polarographic Behavior of Some Alkyl and Aryl Nitrosamines" by G. C. Whitnack, R. D. Weaver, and H. W. Kruse (Abstract No. 91)

2:30 P.M.—"A Polarographic Study of Sodium-iodomethane Sulfonate in Various Media" by M. J. Allen and V. J. Powell (Abstract No. 92)

3:00 P.M.—"Polarographic Behavior of Iodinated X-Ray Contrast Agents" by Peter Kabasakalian (Abstract No. 93)

3:30 P.M.—"Polarography of Organo Tin Halides" by C. M. Wheeler, Jr. (Abstract No. 94)

4:00 P.M.—"Polarographic Behavior of Steroids" by Peter Kabasakalian (Abstract No. 95)

Electro-Organic (cont'd)
Thursday, October 10, 1957
Polarography
with S. Wawzonek presiding
(EMPIRE STATE ROOM)

9:00 A.M.—"Correlation of Polarographic Half-Wave Potentials with Nuclear Magnetic Resonance 'Chemical Shifts'" by C. E. Bennett and P. J. Elving (Abstract No. 96)

9:30 A.M.—"Correlation of Polarographic Half-Wave Potentials of Organic Compounds" by P. J. Elving and C. E. Bennett (Abstract No. 97)

10:00 A.M.—Round-table discussion on the **Application of Polarographic Techniques in the Pharmaceutical Field,** with M. J. Allen as Chairman, and Mr. Peter Kabasakalian.

ELECTROTHERMICS AND METALLURGY

Monday, October 7, 1957
General Session
with G. M. Butler presiding
(NEW YORK ROOM)

2:00 P.M.—"Equilibria between Titanium Metal and Solutions of Titanium Dichloride in Fused Sodium Chloride" by K. Komarek and P. Herasymenko (Abstract No. 98)

2:30 P.M.—"Reaction Kinetics of the Nitriding of Titanium Dioxide" by D. L. Douglass, J. H. Borden, and G. R. St. Pierre (Abstract No. 99)

3:00 P.M.—"Continuous Electrolytic Process for the Production of High Purity Beryllium Metal" by S. J. Morana (Abstract No. 100)

3:30 P.M.—"Equilibrium Reduction of Tungsten Oxides by Hydrogen" by R. C. Griffis (Abstract No. 101)

Electrothermics and Metallurgy (cont'd)
Tuesday, October 8, 1957
Ferroalloys and Slags
with E. T. Johnson presiding
(GEORGIAN ROOM)

9:15 A.M.—Opening remarks by E. T. Johnson

9:25 A.M.—"A Review of the Uses and Markets for Ferroalloys" by R. W. Hale (Abstract No. 102)

10:05 A.M.—"Metallurgical Design of Submerged Arc Furnaces" by W. M. Kelly (Abstract No. 103)

10:45 A.M.—"Electric Smelting of Low Grade Nickel Ores" by L. H. Banning (Abstract No. 104)

11:15 A.M.—"Dissociation and Electrical Conductivity of Molten Silicates" by Axel Wejnarth (Abstract No. 105)

Electrothemics and Metallurgy (cont'd)
Wednesday, October 9, 1957
with A. C. Haskell presiding
(EMPIRE STATE ROOM)

9:30 A.M.—"Ferroalloys from Low Grade Ores by the Udy Processes" by M. C. Udy and M. J. Udy (Abstract No. 106)

10:00 A.M.—"Experimental Production of Iron, Silicospiegeleisen, and Portland Cement from a Low Grade Manganiferous Iron Ore" by R. A. Campbell, G. N. Banks, and R. R. Rogers (Abstract No. 107)

10:30 A.M.—"Small Single Phase, Dry-Top Electric Furnace for Experimental Smelting of Manganese Ores" by D. D. Blue (Abstract No. 108)

11:00 A.M.—"Electrodeposition of High Purity Chromium" by F. E. Block, P. C. Good, and G. Asai (Abstract No. 109)

ABSTRACTS

In the Index to Authors, the Abstract Number is the number listed in the right-hand column.

BATTERY

Abstract No. 1

The Anodic Oxides on Lead

Jeanne Burbank, U. S. Naval Research Lab., Washington 25, D. C.

The anodic oxides formed on Pb under varying potential and pH were identified by x-ray and electron diffraction. The potential-pH phase diagram of Pb has been expanded by definition of the crystalline phases present as electrode species. The lamellar nature of the anodic product formed on Pb under conditions obtaining in the Pb-acid cell is interpreted on the basis of the diagram.

Abstract No. 2

The Electrochemical Properties of PbO_2 and the Anodic Corrosion of Lead and Lead Alloys

Paul Ruetschi, Research Dept., Electric Storage Battery Co., P. O. Box 5723, Philadelphia 20, Pa.

Since the electric and electrochemical properties of the alpha and beta forms of PbO_2 depend on their oxygen lattice defects, x-ray diffraction patterns and electrode potential measurements have been made on a series of lead oxides formed by thermodecomposition of PbO_2.

Anodic polarization of lead in H_2SO_4 under conditions of oxygen evolution leads to layers of α-PbO_2 with excess oxygen in the surface. The amount of excess oxygen is related to oxygen overvoltage and corrosion. This study has also included a large series of lead alloys.

Abstract No. 3

The Correction of X-Ray Diffraction Powder Photographs for Highly Absorbing Samples*

P. E. Jensen and **E. J. Ritchie,** Eagle-Picher Research Labs., Joplin, Mo.

The interpretation of x-ray diffraction powder photographs is based on the precise determination of the line positions. From highly absorbing materials, as lead oxide, the diffraction pattern arises from a very thin surface layer and with a cylindrical sample the diffraction line is displaced a variable amount at different 2θ angles. A method of line measurement and correction was developed which yields line position data of higher precision than the usual method of correcting for sample diameter.

* This work sponsored by Office of Naval Research Contract number Nonr 1513(00).

Abstract No. 4

The Unit Cell of Yellow Litharge*

P. E. Jensen and **E. J. Ritchie,** Eagle-Picher Research Labs., Joplin, Mo.

Observed physical properties of various yellow litharge preparations suggest a much larger unit cell of perhaps different symmetry at high temperatures but for which the usually accepted orthorhombic cell is a related substructure at room temperature. It appears probable that the large unit cell may persist at room temperature to a varying degree determined by impurities and the history of the sample.

* This work sponsored by Office of Naval Research Contract Nonr 1513(00).

Abstract No. 5

Changes in Positive Active Material Density during Various Conditions of Service

J. F. Dittmann and **J. F. Sams,** Eagle-Picher Research Labs., Joplin, Mo.

Observations made on the lead-acid battery indicated that changes were occurring in the apparent density of the positive active material during service. To determine the extent of these density changes, measurements have been conducted during and under all conditions of testing. The apparent density of the positive active material has been found to decrease regardless of active material shedding. This finding may explain many observed performance characteristics of the lead-acid battery.

Abstract No. 6

The Action of Silver and Cobalt at the Positive Plate of the Lead-Acid Battery

J. J. Lander, Electric Auto-Lite Co., Toledo 1, Ohio

The electrochemical action of Ag and Co at the positive plate of a Pb-

acid battery is explained. Corrosion rates of positive grids have been determined over the range of voltages which the positive plate can experience in service and on the SAE Overcharge Test. The protective effect of Ag and Co on the SAE test follows from the explanation and the corrosion data. These results are discussed in terms of positive grid life in passenger car service.

Abstract No. 7

Influence of Positive Grid Alloy and Element Design on Battery Performance

H. Stoertz, Research Dept., Electric Storage Battery Co., P. O. Box 5723, Philadelphia 20, Pa.

While such additives as As and Ag enhance the corrosion resistance of positive grids, selection of the proper Sb content is likewise important and contributes to battery performance by means of increased life and lower negative sulfation. The maximum benefit residing in the use of lower Sb content as well as added As and/or Ag can be obtained only when positive active material is prevented from shedding. This can be accomplished by selection of suitable plate construction or suitable element design.

Abstract No. 8

Design and Quality Control in the Battery Industry through Microscopy

A. C. Simon and **E. L. Jones,** U. S. Naval Research Lab., Washington 25, D. C.

Examples are presented to show how the microscope may be used in the study of all parts of the storage cell. It is shown that a specialized technique of battery examination is available that could be applied to quality control in battery manufacture and also serves as a useful tool in research and development.

Abstract No. 9

Designing for Quality

H. J. Strauss, Research Dept., Electric Storage Battery Co., P. O. Box 5723, Philadelphia 20, Pa.

Modern trends for product engineering have found that they must frequently abandon the classical concepts on which design tolerances and variations are predicated. For example, the principle that assemblies must be satisfactory if all parts, except one, are at one end of the tolerance with the single part at the other end, can result in costly assemblies whose performance can be severely substandard. Modern concepts require that such assemblies actually do not go together satisfactorily, so as to preclude their introduction into the market. Batteries are particularly amenable to these concepts in that they represent "stacked" assemblies whose tolerances must be carefully balanced out. The principles on which this can be done and the disposition of unsatisfactory assemblies are discussed as related specifically to battery design.

Abstract No. 10

Design Factors for Nickel-Cadmium Batteries

Arthur Fleischer, R. E. Rockey, and **G. B. Ellis,** Nickel Cadmium Battery Corp., Easthampton, Mass.

Battery design is influenced to a large extent by end use and application. The element design is the basic feature in defining the electrical performance. The design of tabs, internal connectors, terminal posts, glands, gas space, sediment space, intercell connectors, and other constructional features is also important for ease of maintenance and long battery life. These features, too often taken for granted, will be illustrated for pocket type and sintered plate-type Ni-Cd batteries.

Abstract No. 11

Improvement in Negative Plate Performance

Arthur Fleischer, Nickel Cadmium Battery Corp., Easthampton, Mass.

Cycling characteristics of the negative Cd electrode have been improved by the discovery of two types of expander, namely, alkali-soluble cellulose derivatives and indium. Experimental studies were based on the repeated charging and discharging of cells with three-plate elements in which the negative electrode was capacity limiting. Conditions for capacity loss or maintenance were defined. Under the conditions of operation showing capacity loss for Cd electrodes of previously known compositions, the incorporation of the new expanders prevents capacity loss and improves performance.

Abstract No. 12

Cinemicrography of the Freezing Process in Lead-Antimony Grid Alloys

A. C. Simon and **E. L. Jones,** U. S. Naval Research Lab., Washington 25, D. C.

The actual freezing process occurring in Pb-Sb alloys is illustrated. Supercooling of the eutectic and a preferred dendritic growth of Sb in the surface layer are found to occur as was postulated previously from theoretical considerations.

Abstract No. 13

Measurement of the Internal Resistance of Standard Cells

G. D. Vincent, Standard Cell Dept., The Eppley Lab., Inc., Newport, R. I.

The internal resistance of standard cells is measured by several methods. For new cells in good condition, the results by different methods are in closer agreement than for old cells or those which have been subjected to high temperatures or current passage. The use of the apparent difference in internal resistance by different methods of measurement as a criterion of the stability of the emf of a standard cell is examined.

Abstract No. 14

A New Approach to Resistance Measurements of Dry Cells

R. J. Brodd, National Bureau of Standards, Washington 25, D. C.

A new technique for measuring resistance of Leclanché cells is described. The resistance of Leclanché cells was measured as a function of size, residual capacity, and current drain.

Abstract No. 15

Formation of Manganese (II) Ion in the Discharge of the Manganese Dioxide Electrode, II. Effect of Volume and pH of Electrolyte

W. C. Vosburgh, Mary Jo Pribble, Akiya Kozawa, and **Ahmed Sam,** Dept. of Chemistry, Duke University, Durham, N. C.

Discharge of the MnO_2 electrode at pH 5-8 is known to give Mn^{++} in solution as well as a lower oxide. When the volume of electrolyte is varied, the amount of Mn^{++} is practically independent of volume. It decreases as the pH increases, becoming small at pH 8. The reaction of lower oxides with electrolytes shows a similar relation to volume and pH. These results aid in understanding the discharge process.

Abstract No. 16

The Relation of the Conditions of Electrodeposition of Manganese Dioxide to the Discharge Characteristics

Akiya Kozawa and **W. C. Vosburgh,** Dept. of Chemistry, Duke University, Durham, N. C.

Electrodes were prepared by electrodeposition of MnO_2 at various temperatures and current densities, or with NH_4^+, K^+, Zn^{++}, Mg^{++}, or Al^{+++} in the plating bath. Overpotentials in acid electrolyte, discharge curves in NH_4Cl electrolyte, and the Mn^{++} in solution in the latter case were determined. Differences could be explained as resulting from differences in structure, thickness, or surface area, the latter measured by adsorption of Zn^{++}.

Abstract No. 17

Studies on the Vapor Pressure and the Density of Electrolytes for Dry Cells

Kumazo Sasaki, Dept. of Applied Chemistry, Faculty of Engrg., Nagoya University, Furo-Cho, Chikusa-ku, Nagoya, Japan

Measurements have been made of vapor pressures and densities, as function of temperature at 10°, 18°, 25°, and 32°C, for 50 sample solutions consisting of various mole ratios of NH_4Cl (0~15 mole/kg H_2O) and $ZnCl_2$ (0.5~9.5 mole/kg H_2O). These data, with the vapor pressure and change of specific volume, allow calculations of water activities and salt errors, which appear in the case of determining pH value of the mixed solutions.

Abstract No. 18

A Magnesium Sea-Water Battery

J. J. Shotwell and **R. C. Kirk,** Dow Chemical Co., Texas Div., Freeport, Texas, and Midland Div., Midland, Mich., respectively.

Performance characteristics for a magnesium anode air-depolarized sea-water battery are described. Voltage and current output and anode efficiency remained favorable through long periods of sustained discharge. The battery appears to have utility for low cost unattended operation of off-shore equipment such as instruments and signal lights.

Abstract No. 19

Ammonia Vapor-Activated Reserve Batteries*

H. S. Gleason and **J. M. Freund**, Eastman Kodak Co., Rochester, N. Y., and **L. J. Minnick** and **W. F. Meyers**, G. & W. H. Corson, Inc., Plymouth Meeting, Pa.

A new type of reserve battery is described. In storage, the solvent for the electrolyte, liquid ammonia, is kept separate from the dry, deliquescent solute. On activation, ammonia vapor is released to condense rapidly in the cells and energize the battery. A large number of practical cells can be built using this principle. Characteristics of several are discussed. Some of the properties of electrolytes in liquid ammonia are also presented.

* This work sponsored by the Dept. of Defense under various contracts.

Abstract No. 20

A Unique Dry Battery

H. B. Reed, Jr., and **M. B. Goldberg**, Naval Ordnance Lab., White Oak, Silver Spring, Md.

A unique dry battery has been developed at the Naval Ordnance Lab. Its greatest asset is storageability under adverse conditions. A storage life of ten years or more is anticipated. One year of storage at 165° has not affected the capacity of this battery. An active life of over 3½ years has been observed. The battery is readily rechargeable. As many as 36 charge-discharge cycles have been measured with little change in capacity. The fully charged unit employs the following electrochemical system Pb/KOH/Ag_2O.

Abstract No. 21

Indium as an Anode Material

T. L. Boswell, Elgin National Watch Co., Elgin, Ill.

Indium and indium-bismuth alloys are evaluated as energy producing electrodes for use in small sealed cells. Important electrochemical characteristics of these materials are compared to the commonly used electrode metals and the areas in which significant advantages and disadvantages exist are indicated. The performance of these electrodes has been measured in small sealed cells against a mercuric oxide cathode. Results are discussed in relation to current-carrying ability, electrical capacity, and voltage stability.

Abstract No. 22

Halogen-Activated Solid Electrolyte Cell

J. L. Weininger, Research Lab., General Electric Co., P. O. Box 1088, Schenectady, N. Y.

A new type of silver-halide solid-electrolyte cell consists of a small bead of silver halide with tantalum and silver wires, cathode and anode, respectively. The mechanism of the electrochemical reaction has been determined. When exposed to halogen vapor, the cell is a promising primary cell for elevated temperatures. With silver iodide as electrolyte, the cell can be recharged several times.

Abstract No. 23

An Investigation of Some New Cathode Depolarizer Materials

A. B. Tripler, Jr., and **L. D. McGraw**, Electrochemical Engrg. Div., Battelle Memorial Institute, Columbus 1, Ohio

The electrochemical behavior and charge retention of manganic phosphate, barium ferrate, and chloranil (tetrachloroquinone) are described. The electrochemically active materials, mixed with carbon, have observed capacities of 8, 4, and 6 w-min/g, respectively, when discharged as cathodes at rates of 200 ma/in.^{2} for the first two, and 100 ma/in.^{2} for the third. The kinetic limitations for the electrode processes are discussed.

Abstract No. 24

Investigations of Electrochemical Characteristics of Organic Compounds, I. Aromatic Nitro Compounds

R. Glicksman and **C. K. Morehouse**, RCA Labs., Radio Corp. of America, Princeton, N. J.

A study of the electrochemical characteristics of aromatic nitro compounds shows that the cathode potential of these compounds during current flow is dependent on the type and position of substituted groups on the aromatic ring, as well as the composition and pH of the electrolyte. Coulometric reduction studies of various mono and dinitro aromatic compounds indicate reduction of these compounds takes place to the amino stage, with a resultant 6 electron change per $-NO_2$ group, at electrode efficiencies of 70-90%.

Abstract No. 25

Nitro Aromatic-Magnesium Dry Cells

C. K. Morehouse and **R. Glicksman**, RCA Labs., Radio Corp. of America, Princeton, N. J.

Many aromatic nitro compounds when coupled with a magnesium anode and a $MgBr_2$ electrolyte give dry cells with practical features, the discharge characteristics being dependent on the type of nitro aromatic compound used as a cathode. The meta dinitrobenzene-magnesium dry cell has been thoroughly characterized, and shown to have a favorable shelf life, and give greater watt-hour capacities per unit of weight and volume than the commercial Leclanché cell.

Abstract No. 26

Investigations of Electrochemical Characteristics of Organic Compounds, II. Aromatic Nitroso Compounds

R. Glicksman and **C. K. Morehouse**, RCA Labs., Radio Corp. of America, Princeton, N. J.

This study has shown that C-nitroso organic compounds operate at a higher discharge potential than their corresponding nitro organic compounds, as well as the various oximes, N-nitroso, and N-oxide organic compounds tested. A limited study of the various C-nitroso organic compounds has shown that the discharge potential is pH dependent, and is affected by the type and position of the substituted group on the aromatic ring.

Abstract No. 27

Nitroso Aromatic-Magnesium Dry Cells

C. K. Morehouse and **R. Glicksman**, RCA Labs., Radio Corp. of America, Princeton, N. J.

Dry cells have been made using various C-nitroso aromatic compounds and cathodes coupled with a magnesium anode. These cells, which operate at higher discharge potentials than corresponding nitro aromatic-magnesium dry cells, have characteristics which are dependent on the type of nitroso compound used as a cathode. The p-nitrosodimethylaniline-magnesium dry cell has been fully characterized, and shown to operate at a flat voltage level between 1.3 and 1.4 v, and give greater watt-hour capacities per unit of weight and volume than the commercial Leclanché dry cell.

Abstract No. 28

N-Halogen Organic Reserve Batteries

G. S. Lozier, L. H. Cutler, and **C. K. Morehouse**, RCA Labs., Radio Corp. of America, Princeton, N. J.

N,N'dichlorodimethylhydantoin, trichloromelamine, hexachloromelamine, trichloroisocyanuric acid, and dichloroisocyanuric were found to be the most promising N-halogen organic compounds for use in the design of a high capacity reserve battery. Experimental N-halogen organic-magnesium reserve cells have been constructed, using a titanium positive electrode and a dry formed cathode. These cells have a capacity of 1.5-1.6 amp-hr, and give capacities of over 50 whr/lb and 2 whr/ in.^{3}, allowing a 20% voltage drop.

CORROSION

Abstract No. 29

The Germanium-Water-Oxygen System: Kinetics of the Dissolution Process*

W. W. Harvey and **H. C. Gatos**, Lincoln Lab., Massachusetts Institute of Technology, Lexington, Mass.

The reaction of crystallographically oriented Ge surfaces with water has been shown to depend primarily on concentration of dissolved oxygen and temperature. It is not affected significantly by the concentration of mobile carriers in Ge. Thus, illumination has no effect on the dissolution rate. Dissolution rates have been measured for single-crystal specimens of various orientations, the observed order being {100} > {110} > {111}. A mechanism for the reaction is proposed.

* The research reported in this document was supported jointly by the Army, Navy, and Air Force under contract with M.I.T.

Abstract No. 30

Oxidation of Copper Single Crystals in Oxygen-Saturated Water at Room Temperature*

Jerome Kruger, U. S. Dept. of Commerce, National Bureau of Standards, Washington 25, D. C.

Studies of the oxide films formed on the surfaces of Cu single crystals exposed under rigidly controlled conditions to high purity water satu-

* This work is supported in part by the Corrosion Research Council.

rated with oxygen at room temperature are described. The influence of crystallographic orientation of the reacting surface, presence of CO_2, and illumination by white light on relative rate of film growth, nature of oxide, oxide morphology, and metal-oxide epitaxy were investigated.

Abstract No. 31

Metal-Water Reactions, IV. Kinetics of the Reaction between Calcium and Water Vapor

H. J. Svec and **Charles Apel,** Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa

Calcium metal was reacted with water vapor in the temperature range 20°-70°C and at water vapor pressures of 18-93 mm Hg. The experiments indicated that the only products were calcium hydroxide and hydrogen and that the reaction proceeded according to the equation

$$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$$

A manometric study of the reaction showed that it followed the logarithmic rate law,

$$W = K \log (1 + 0.45t)$$

The rate constant K was observed to be linearly dependent on water vapor pressure below 70°C and to decrease with increasing temperature in the range 20°-50°C. At 70°C the rate constant was observed to be independent of water vapor pressure. The activation energy was found to be —7.52 kcal/mole in the pressure dependent range. Temperature and water vapor pressure were related to the rate constant K in its pressure dependent ranges and the following expression fits the data for water vapor pressures greater than 10 mm Hg:

$$K = 2.57 \times 10^{-6} (P—10)\, e^{3700/T}$$

Abstract No. 32

Metal-Water Reactions, V. Kinetics of the Reaction between Magnesium and Water Vapor

H. J. Svec and **D. S. Gibbs,** Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa.

The rate of reaction between magnesium and water vapor was studied in the temperature range between 425° and 575°C and in the water vapor pressure range between 31 and 208 mm Hg. The reaction took place according to the linear rate law. Rate constants were found to be linearly dependent on the water vapor pressure. The activation energy for the reaction was found to vary with both temperature and water vapor pressure, increasing as the temperature was increased and the water vapor pressure was decreased. This type of variation is explained on the basis of a change from a surface to a vapor pressure of magnesium metal in the temperature range between 500° and 600°C.

Abstract No. 33

Electrochemical Polarization, III. Further Aspects of the Shape of Polarization Curves

Milton Stern, Metals Research Labs., Electro Metallurgical Co., P. O. Box 580, Niagara Falls, N. Y.

The shape of electrochemical polarization curves is discussed for systems containing more than two oxidation-reduction reactions. Conditions were selected which parallel those found in practice for corroding systems. Situations are described where measured Tafel parameters have no direct relationship to the parameters of any of the oxidation-reduction reactions. The analysis shows the complexity of polarization measurements and indicates the care which must be taken if such measurements are to be interpreted quantitatively.

Abstract No. 34

Electrochemistry of Magnesium

G. R. Hoey and **M. Cohen,** National Research Council, Ottawa, Canada

The effect of current density, pH, and temperature on the anodic behavior, cathodic behavior, and corrosion of Mg in aqueous solutions has been studied. A tentative mechanism for the anodic oxidation of Mg was postulated. Local corrosion and undermining of metallic Mg at the anode are appreciable and may, in fact, account for the observed low anodic current efficiencies of Mg. An intergranular type of corrosion occurs at cathodically polarized Mg at the elevated temperatures. A hydrogen embrittlement theory was proposed to explain intergranular cathodic corrosion. Anodic and cathodic polarization curves of Mg are reported.

Abstract No. 35

Use of High Purity Aluminum and Its Alloys in Controlling the Corrosion of Magnesium Alloys, I. The Galvanic Compatibility of Aluminum Alloys with Magnesium Alloys

M. R. Bothwell, Chemical Section, Metallurgical Lab., The Dow Chemical Co., Midland, Mich.

Its extremely high hydrogen overvoltage and freedom from depolarization by dissolved oxygen make high purity Al almost completely compatible with Mg alloys in saline environments. Alloying the Al with small amounts of low overvoltage metals such as Fe, Cu, and Ni seriously decreases this compatibility, but the tolerance for these constituents is greatly increased by alloying with Mg.

Abstract No. 36

Use of High Purity Aluminum and Its Alloys in Controlling the Corrosion of Magnesium Alloys, II. The Protection of Magnesium Alloys by Aluminum

M. R. Bothwell, Chemical Section, Metallurgical Lab., The Dow Chemical Co., Midland, Mich.

Because of its remarkable galvanic compatibility and excellent resistance to corrosion in most service environments, high purity Al is an extremely promising coating material for Mg alloys. The corrosion resistance of these coated composites is very sensitive to low overvoltage impurities in the coating during exposure to NaCl solution and less sensitive during exposure to sea water which buffers the system at a lower pH and thus better controls alkaline attack of the coating.

Abstract No. 37

Reaction of Aluminum and Carbon Tetrachloride, I

J. D. Minford, M. H. Brown, and **R. H. Brown,** Research Labs., Aluminum Co. of America, New Kensington, Pa.

Many Al alloys are severely corroded by boiling CCl_4. The major products of the reaction are aluminum chloride and hexachloroethane. The presence of anhydrous aluminum chloride accelerates the reaction. A number of chemical agents can retard this reaction apparently by combining with aluminum chloride as it is produced. The reaction of Al alloys drops off rapidly as the Mg content increases.

Abstract No. 38

Reaction of Aluminum and Carbon Tetrachloride, II

R. H. Brown, E. H. Cook, M. H. Brown, and **J. D. Minford,** Research Labs., Aluminum Co. of America, New Kensington, Pa.

The mechanism of the reaction between Al and boiling CCl_4 appears to be electrochemical. Conductivity measurements indicate that the reaction starts as soon as the Al is exposed to the boiling solution. The increase in conductivity with time is caused by the presence of $AlCl_3$ and parallels the increase in weight per cent Al as the reaction proceeds. The application of a cathodic current prevents attack of an Al specimen, indicating that the initial attack is caused by the presence of an ionic species. Trace amounts of the reaction product hexachloroethane were produced electrochemically in the absence of any Al.

Substances that retard the reaction apparently function by forming inactive complexes with the $AlCl_3$. The rate-determining step in the reaction does not appear to involve free radicals since the majority of the effective inhibitors failed to react with known free radicals.

Abstract No. 39

Accelerated Corrosion in Aluminum-Silver Alloys

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In the presence of photographic developer, Al-rich Al-Ag alloys corrode in air by a mechanism that is accelerated by the tendency of the developer to reduce the precipitated compound $AlAg_2$ to Ag. This reduction occurs only at preferred sites in pure $AlAg_2$ but is quite general in the precipitated compound.

Abstract No. 40

Room Temperature Tarnishing of Silver in Bromine and Iodine

J. L. Weininger, Research Lab., General Electric Co., P. O. Box 1088, Schenectady, N. Y.

Pure Ag was tarnished in an atmosphere of iodine or bromine vapor at room temperature. This resulted in impervious halide surface layers, from which tarnishing rates could be deduced by means of a new photomicrographic technique. It was found that the parabolic rate law,

with diffusion being the rate-determining step, also holds at room temperature. The effect of pretreatment of Ag on the rate of halogenation is discussed.

Abstract No. 41

Effect of Steel, Passivating Solution, and Corrosive Media Variations on the Electrochemical Method of Detecting Hydrogen Diffusion through Steel

T. J. Butler, Applied Research Lab., U. S. Steel Corp., Monroeville, Pa.

If one side of a steel specimen corrodes in a media in which the formation of hydrogen is at least part of the cathodic reaction, some of the hydrogen in the atomic state will diffuse through the steel. This diffused hydrogen can destroy the passivity imparted to another surface of the steel specimen, as is evidenced by a change in potential of the passive surface from noble to active values. Passivating solutions (such as dichromates, permanganates, NaOH, concentrated HNO_3, and some salt solutions) and hydrogen-producing corroding media (such as various acids, KCl, sodium sulfate, and distilled water) were studied. Steel specimens were chosen from lots of tin-plate steels, stainless steels, and enameling steels.

Abstract No. 42

Cathodic Reduction of Oxide Films on Iron, II. Determination of α-Fe_2O_3 and Fe_3O_4

K. H. Buob, A. F. Beck, and **M. Cohen,** National Research Council, Ottawa, Canada

A study of the cathodic reduction of α-Fe_2O_3 on Fe has been made with the object of using the technique for the accurate determination of both the α-Fe_2O_3 and Fe_3O_4 formed during the oxidation of Fe. The films were examined after oxidation and after various stages of cathodic reduction. Examination was made by weight change, electron diffraction, x-ray diffraction, and chemical analysis of the films. Some evidence for the existence of a thin layer of α-Fe_2O_3 between the layers of Fe_3O_4 and α-Fe_2O_3 was found. A standard pattern for Fe_3O_4 was obtained.

Abstract No. 43

Chemical Factors Affecting Stress Corrosion Cracking of 18-8 Stainless Steels

H. H. Uhlig and **John Lincoln, Jr.,*** Corrosion Lab., Dept. of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

Fundamental studies show that transgranular stress corrosion cracking of 18-8 in boiling 42% $MgCl_2$ is accelerated by additions of acid, and decelerated by additions of alkali. Oxygen or other depolarizers are accelerators. Pre-exposure of unstressed specimens to the test solution slightly decreases cracking time of subsequently stressed specimens. Cracks propagate at the rate of 0.5-1 cm/hr. Sizeable pits are not necessary to initiate cracks in $MgCl_2$, but in NaCl solutions they act as reservoirs for concentrated $FeCl_2$ solution, which like $MgCl_2$ causes rapid cracking. Cracking time was found independent of rate of stressing, and was decreased by cold work. Stress-relief anneal at 375°C for 2 hr did not avoid susceptibility. Cracking can be prevented by cathodic protection at a C.D. greater than 0.03 ma/cm^2.

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Abstract No. 44

The Effect of Gamma Irradiation on the Potential Behavior of Platinum and Stainless Steel Electrodes

W. E. Clark, Chemistry Div., Oak Ridge National Lab., P. O. Box P, Oak Ridge, Tenn.

Electrode potentials of stainless steel and of Pt in 0.1*N* H_2SO_4 at 85°C were measured in a gamma source giving a dose rate of 8.5 x 10^{17} ev/g water-minute. The potential behavior of the electrodes is believed to depend on the balance between oxidizing and reducing species in solution which is determined by the products of the radiolysis of water and their reactions with each other and with the particular atmosphere employed.

Abstract No. 45

The Diffusion of Oxygen in Zirconium

J. P. Pemsler, Nuclear Metals, Inc., Cambridge, Mass.

The diffusion of oxygen in zirconium has been determined at 400°-585°C by measuring the rate at which the metal dissolves anodically deposited oxide films. The diffusion coefficient depends on grain orientations, varying by a factor of two among different orientations. Macroscopically observed average values obey the equation $D_{cm^2/sec} = 9.4 \exp[-(51{,}780 \pm 220)/RT]$. The oxidation rate has an orientation dependence similar to the diffusion coefficient, so that adjacent grains in a matrix grow oxide at greatly different rates.

Abstract No. 46

Formation Fields and Current Efficiencies in the Anodic Oxidation of Zirconium: A Direct Comparison of High Potential Formation Fields with Those Derived from Low Potential Charging Curves

G. B. Adams, Jr., T. S. Lee (present address: Research Labs., Westinghouse Electric Corp., Pittsburgh 35, Pa,), and **Pierre Van Rysselberghe** (present address: Dept. of Chemistry, Stanford University, Stanford, Calif.) Dept. of Chemistry, University of Oregon, Eugene, Oreg.

Formation fields at selected constant currents were obtained from high potential unitary formation rates and polarographic current efficiency measurements carried out over the potential range, 20-130 v. These values are compared with formation fields derived from low potential unitary formation rates alone, in the potential range below 2 v.

Results are reported for abraded Kroll process metal at 750 μa/cm^2, for abraded and chemically polished iodide process metal at 100 and 750 μa/cm^2, and at 100 μa/cm^2, respectively. Ionic current efficiencies are reported for several current densities in the high potential range and for the low potential localized oxygen evolution process.

Abstract No. 47

The Reaction of Zirconium with Water Vapor at Subatmospheric Pressures

M. W. Mallett, W. M. Albrecht, and **R. E. Bennett,** Battelle Memorial Institute, 505 King Avenue, Columbus 1, Ohio

The reaction of iodide zirconium with water vapor at 33 mm of mercury pressure was investigated in the range 300°-600°C. The rates follow a cubic law. The cubic rate constant in $(\mu g/cm^2)^3/sec$ is $k = 6.71 \times 10^3 \exp(-29{,}700/RT)$ where 29,700 = 700 cal/mole is the activation energy. Reaction films of monoclinic ZrO_2 are *N*-type semiconductors. Therefore, it is concluded that the mechanism of film formation is the same as that for the zirconium-oxygen reaction.

Abstract No. 48

Reaction of Hydrogen with Preoxidized Zircaloy-2

E. A. Gulbransen and **K. F. Andrew,** Research Labs., Westinghouse Electric Corp., Pittsburgh 35, Pa.

The permeability of preformed oxide films to hydrogen at 300°-400°C was studied. Two types of reactions were observed. If the oxide film was permeable, a general reaction occurred with the formation of zirconium hydride phases on the surface. If the oxide film was relatively impermeable, reaction occurred at the edges of the sample where defects probably exist in the oxide. The reaction starts at localized areas and spreads through the metal with hydride continually spalling from the metal.

Abstract No. 49

The Effect of Pre-Oxidation in Oxygen on the Steam Corrosion Behavior of Zircaloy-2

D. E. Thomas and **S. Kass,** Atomic Power Div., Bettis Field, Westinghouse Electric Corp., P. O. Box 1468, Pittsburgh 30, Pa.

The effect of pre-oxidation in dry oxygen gas on the corrosion behavior of Zircaloy-2 and unalloyed Zr in steam was investigated. In the case of Zircaloy-2 pre-oxidation has no effect on corrosion behavior, the kinetics being the same whether all or part of the total exposure is in oxygen. A transition in kinetics from quasi-cubic to linear occurs in the corrosion of Zircaloy-2 in either medium, indicating that the transition is not associated with corrosion product hydrogen. On the other hand, unalloyed Zr shows neither transition nor breakaway (spalling) when exposed to oxygen, and exhibits breakaway on exposure to steam whether pre-oxidized or not, suggesting that breakaway is associated with corrosion product hydrogen. The phenomena of breakaway and transition are shown to be distinctly different.

Abstract No. 50

Electrolytic Etching of Dense Tantalum

A. L. Jenny and **R. A. Ruscetta,** Capacitor Dept., General Electric Co., Hudson Falls, N. Y.

Dense Ta in the form of 0.0005 in. thick foil can be electrolytically

etched in substantially nonaqueous systems containing a variety of solutes. Magnification of the surface area is determined by capacitance measurements and described as a function of polarization voltage. The effects of concentration of solute, anodic current density, operating temperature, moisture content of bath, and condition of the metal surface are described.

Abstract No. 51

Metallographic Manifestations of the Air Oxidation of Tantalum at 750°C

Robert Bakish, Sprague Electric Co., North Adams, Mass.

Experiments describing the air oxidation of Ta at 750°C are presented. The crystallographic factors in the segregation of Ta_2O_5 are presented. A mechanism for the conversion of metal to oxide is proposed.

Abstract No. 52

Nucleation of Crystalline Ta_2O_5 during Field Crystallization

D. A. Vermilyea, General Electric Co., Research Lab., Schenectady, N. Y.

Nucleation during field crystallization of amorphous Ta_2O_5 films occurs at heterogeneities on the metal surface. The time between the application of the field and the appearance of the first crystals corresponds to growth to critical size of a crystal on one of the nucleation sites. The logarithm of the incubation period increases linearly with decreasing electric field at constant temperature. Possible mechanisms for the nucleation of crystals under these conditions are discussed.

Abstract No. 53

Ionic Conductivity of Anodic Films at High Field Strengths: Transient Behavior

D. A. Vermilyea, Research Lab., General Electric Co., Schenectady, N. Y.

Studies of the changes in ionic conductivity of anodic Ta_2O_5 films following rapid changes of applied voltage or following a heat treatment of the film have shown that the activation energy and the activation distance for ionic motion vary with changes in the temperature and electric field strength at which the film is grown. An explanation of these effects in terms of changes in the structure of the film is discussed.

Abstract No. 54

Annealing Anodic Ta_2O_5 Films: Changes in Dissolution Behavior and X-Ray Scattering

D. A. Vermilyea, Research Lab., General Electric Co., Schenectady, N. Y.

When an anodic Ta_2O_5 film is heated to temperatures up to 600°C the rate of dissolution of the film in HF decreases and the x-ray diffraction from the film becomes sharper. It is believed that these changes are the result of changes in local ionic configuration in the film.

Abstract No. 55

Effect of Ultraviolet Irradiation on the Growth of Anodic Ta_2O_5 Films

D. A. Vermilyea, Research Lab., General Electric Co., Schenectady, N. Y.

When a growing anodic Ta_2O_5 film is irradiated with ultraviolet light the film is transformed to a material of different physical and chemical properties, and the film growth is accelerated. The nature of the transformed film and a possible mechanism for the transformation are discussed.

CORROSION - ELECTRODEPOSITION

Abstract No. 56

The Mechanism of Corrosion of Copper-Nickel-Chromium Coatings

H. J. Read, Dept. of Metallurgy, College of Mineral Industries, Pennsylvania State University, University Park, Pa.

The mechanism of selective corrosion of Cu under Ni in Cu-Ni-Cr coatings is explained on the basis of the modern electrochemical theory of corrosion and simple laboratory experiments which simulate conditions that could prevail in the corrosion of practical parts such as automobile bumpers. The interpretation is supported by photomicrographs showing in cross section the progress of corrosion in test bumpers which have been weathered outdoors.

Abstract No. 57

Double Nickel Coatings

B. B. Knapp and **R. J. McKay,** Research Lab., International Nickel Co., Bayonne, N. J.

Composite coatings of Cu and Ni have been used extensively for numerous reasons as an undercoat for a decorative Cr finish. Recently the American Society for Testing Materials, in studying performance tests on electrodeposited coatings, discovered that a coating of two layers of Ni was superior to a single layer and even to a coating of Cu-Ni composite. This paper examines the data on both the preparation and exposure of these coatings and scrutinizes their microstructure to determine if a plausible explanation can be advanced to account for this behavior.

Abstract No. 58

Effects of Acoustical Waves on the Electrodeposition of Chromium*

Joseph Dereska (National Carbon Research Labs., Parma, Ohio), **Ernest Yeager,** and **Frank Hovorka,** Dept. of Chemistry, Western Reserve University, Cleveland, Ohio

The effects of acoustical waves on Cr electrodeposition have been examined at 10 and 260 kc/sec as functions of plating solution formulation, current density, temperature, and acoustical intensity. Some improvements in hardness, porosity, and adhesion were found at both frequencies. The current range of bright deposits is shifted to higher values while grain size is generally decreased. Data for polarization and current efficiencies will also be presented.

*Research partially supported by the Ordnance Corps of the U. S. Army.

Abstract No. 59

Electrodeposition of Chromium Alloys—A Literature Review

Charles Levy, Watertown Arsenal Labs., Watertown, Mass.

Methods have been reported in the periodical and patent literature for electrodeposition of Cr-base alloys. The alloying elements of interest for high temperature protection of materials include W, Mo, Co, Ni, Fe, Ta, and Nb. It is anticipated that further research in this field will yield plating methods which are both practical and economical.

Abstract No. 60

The Protective Value of Tin-Nickel Alloy Deposits on Steel

F. A. Lowenheim, Metal & Thermit Corp., Rahway, N. J., and **W. W. Sellers** and **F. X. Carlin,** International Nickel Co., Bayonne, N. J.

Outdoor exposure tests of the comparative value of the Sn-Ni alloy and conventional Ni/Cr deposits on steel, with and without a copper undercoat, are reported. It is shown that Sn-Ni is comparable in protective value to Ni/Cr, not quite so good in marine but superior in industrial atmospheres. The type of corrosion behavior of the two deposits differs considerably. In general, the protective value of the Sn-Ni deposit is of a high order.

Abstract No. 61

Electrodeposition of Manganese and Manganese Alloys: A Literature Survey

E. L. MacNamara, Ordnance Corps., Frankford Arsenal, Philadelphia, Pa.

Synopses of 62 publications concerning the deposition of Mn and its alloys is presented. Electrolyte formulations, operating conditions, and corrosion data are discussed. Aqueous solutions of manganese sulfate and manganese chloride were in most cases reported as the superior electrolytes. Information on other simple salts was available, but not extensive.

Abstract No. 62

Statistical Designs for Corrosion Testing

W. Rowan, Metal & Thermit Corp., 1700 E. Nine Mile Rd., Detroit 20, Mich.

The field of corrosion testing provides an excellent place for the application of the techniques of statistical design of experiments. The use of these designs in corrosion research can result in more information being gained for a given expenditure of effort or money. This paper discusses the use of factorial designs and fractional replicates. Examples are taken from the field of corrosion testing of electrodeposits.

Abstract No. 63

Comparison of Salt Spray Corrosion Rates for Tin Plated Copper in Different Locations

M. S. Frant, Research Div., AMP Inc., Harrisburg, Pa.

Evidence is accumulating that the salt spray test as defined at present may vary significantly from one part of the country to another. Using a new and apparently reproducible chemical evaluation technique, the corrosion of Sn-plated Cu in different locations is reported as a function of exposure time. Results indicate that the present salt spray specifications do not include all of the variables.

Abstract No. 64

The Performance of Supplementary Chromate Films on Zinc

F. R. Nagley, Dept. of the Navy, Bureau of Ships, Washington 25, D. C., and **K. L. Procter** and **H. L. Katz,** Industrial Test Lab., Naval Shipyard, Philadelphia, Pa.

Ten commercial chromate treatments for Zn plating on steel were evaluated for comparative deterioration resistance in marine environments. Depletion rate of hexavalent Cr and contribution of trivalent Cr to the corrosion inhibiting properties of the films were studied. Determination of hexavalent Cr content and resistance to salt spray were indicated to be suitable as quality control methods. The value of chromate films is depreciated by Zn plating in thickness of 0.0002 in. and less.

Abstract No. 65

ELECTRODEPOSITION

Filamentary Growths on Copper Cathodes

T. C. J. Ovenston, C. A. Parker, and **A. E. Robinson,** Admiralty Materials Laboratory, Holton Heath, Poole, Dorset, England.

An investigation has been made of the filamentary growths, originally described by Gollop, which are produced under certain conditions during Cu plating at low current density. The conditions under which these growths occur have now been defined more clearly and the effect of various types of surface active agents in enhancing or preventing their occurrence has been demonstrated. Possible mechanisms for the formation of the filaments have been discussed.

Abstract No. 66

Microstructure of Copper Electrodeposited on Copper

T. H. Orem, U. S. Dept. of Commerce, National Bureau of Standards, Washington 25, D. C.

Investigation of the microstructure of Cu electrodeposited on Cu has disclosed the following: when the affected surface parallels (110), the electrodeposit and basis metal have identical atomic configurations; when parallel to (111), the configuration of the electrodeposit is both the same as that of the basis metal and as a twin to the close-packed surface plane; when parallel to (001), the electrodeposit is both parallel and twinned with respect to the basis metal.

Abstract No. 67

Electron Microscope Studies on Copper Electrodes in Copper Plating Baths

Shinzo Okada and **Saburo Magari,** Engineering Research Institute, Kyoto University, Kyoto, Japan

In the absence of an addition agent in a sulfate bath, facets parallel to the {210} planes of the base crystal develop on the cathode, and the {210} planes of the single Cu crystal develop on the anode. In the presence of thiourea, deposits are smoother. Thiourea has a deep influence on the microstructure of the single copper crystal anode and the {100} planes develop.

The effect of current density on the surface of each electrode obtained in a cyanide bath is strong, and the surface is smooth and has no characteristic orientation. The crystal structure of the electrode has an influence on the pattern obtained.

Abstract No. 68

The Structure of Electrodeposited Nickel

B. C. Banerjee and **A. Goswami,** National Chemical Lab., Poona-8, India

An electron diffraction study was made on the crystal structure, orientation, and mode of growth of Ni deposits from sulfate-chloride-boric acid and chloride-boric acid baths under various bath conditions. The effect of pH, temperature, concentration, current density, mechanical stirring, etc., and of additions such as hydrogen peroxide, nickel nitrate, and sodium chloride was investigated on polycrystalline substrates. Depending on bath conditions, various preferred orientations (one-degree), mixed or otherwise, were developed and their causes have been discussed in detail. These have also been correlated with the mode of cathodic crystal growth process.

Abstract No. 69

Effect of Magnesium Sulfate on Nickel Plating Baths

Ahmad Geneidy (present address: Cairo University, Cairo, Egypt), **W. A. Koehler,** Dept. of Chemical Engrg., West Virginia University, Morgantown, W. Va., and **Willi Machu,** Dept. of Chemical Engrg., Cairo University, Cairo, Egypt

Magnesium salts have been used as constituents of Ni plating solutions over a period of many years. A careful investigation has been made to determine as far as possible the function of Mg salts in Ni plating solutions and their effect on the electrodeposits. It was found that the addition of Mg salts lowers slightly the deposition and decomposition potentials and cathodic polarization and increases the slope of the cathode potential vs. current density curves. The effect of Mg salts on the structure of the electrodeposited Ni, microscopic, x-ray diffraction, and spectrochemical studies are presented. The effects of Mg salts on cathodic current efficiency, throwing power, mechanical properties, and porosity of the deposit were investigated.

Abstract No. 70

Electroplating of Titanium and Other Polyvalent Metals from Molten Salt Electrolyte

R. S. Dean, W. W. Gullett, and **F. X. McCawley,** Chicago Development Corp., 5810 47th Ave., Riverdale, Md.

Ductile and protective plates of metals of groups IV B, V B, and VI B have been electroplated successfully on ferrous and nonferrous metals in molten electrolytes of the halides of the plated metal and alkali or alkaline earth halides. Electrolytes and mechanism of plating formation are discussed.

Abstract No. 71

The Electrolytic Preparation of Titanium from Fused Salts, I. Preliminary Electrolytic Studies with Diaphragmed Cells

M. B. Alpert, F. J. Schultz, and **W. F. Sullivan,** National Lead Co., Titanium Div., Research Lab., P. O. Box 58, South Amboy, N. J.

Reduced titanium chlorides dissolved in fused alkali and alkaline earth chlorides may be electrolyzed in diaphragmed cells under an inert gas atmosphere to yield ductile titanium as adherent, crystalline deposits. The reduced titanium chlorides are prepared *in situ* by adding $TiCl_4$ through a hollow cathode at a controlled feed to current ratio.

Abstract No. 72

An Evaluation of Some Factors Involved in the Mechanical Testing of Electrodeposits

T. J. Whalen and **H. J. Read,** Dept. of Metallurgy, College of Mineral Industries, Pennsylvania State University, University Park, Pa.

In an evaluation of some of the factors which must be considered in the preparation of specimens for the determination of the strength and ductility of electrodeposits, and in the execution of the tests by the hydraulic-bulge technique, it was found that the nature of the basis metal, both as to composition and metallurgical condition, was relatively unimportant. It makes comparatively little difference in tensile strength whether the deposit is tested in adhesive contact with the basis metal or in the detached state, providing that the deposit thickness and the basis metal thickness are about the same. The strain rate is unimportant, but hydrogen in the deposits may affect the results considerably.

Abstract No. 73

Some Testing Cells for the Study of Electroplating Devices

J. K. Skwirzynski and **M. Huttly,** Marconi's Wireless Telegraph Co., Ltd., Baddow Res. Labs., West Hanningfield Rd., Great Baddow, Chelmsford, Essex, England

The complete theoretical treatment is given for two kinds of cells, both of which are shown to yield a reasonably linear current density distribution along the cathode. The actual value of the current densities

can be ascertained directly from the total current fed into the cell. The first cell is very similar to that proposed by Hull, i.e., trapezoidal in shape, the angle of the slanting side being 45°. The electrodes can be placed either along the parallel sides of the cell or, as first suggested by Hull, along the other two sides, when a singularity of the current density appears on the slanting electrode. In both cases the current density may be arranged to be very nearly linear over almost two thirds of the length of the cathode.

The second cell is triangular in shape; the cathode is placed along the base of a 45° isosceles triangle, whereas the anode occupies a part of one of the other sides. The current density distribution along the cathode has almost a triangular shape with good linearity.

Abstract No. 74

Electrolytic Metal Powders—Production and Applications

K. H. Roll, Metal Powder Association, 130 W. 42 St., New York 36, N. Y.

Current production, imports, and production capacities for electrolytic iron powders and electrolytic copper powders are discussed as well as applications and quantities of powder used. A brief description of other methods of producing metal powders and comparative characteristics are given.

Abstract No. 75

Electrodeposition of Powders for Powder Metallurgy

C. L. Mantell, Dept. of Chemical Engrg., Newark College of Engineering, Newark, N. J.

A large number of articles are made by powder metallurgical methods from electrolytically reduced powders. In powder production, cathode current densities are much higher than those of refining; loosely adherent deposits are produced. These are dried, surface oxides removed and classified by screening. Important electrolytic powders are those of Cu, Fe, Ni, Zn, some alloys, as well as duplexes. Operating details are reviewed.

Abstract No. 76

Electrolytic Iron Powders—Production and Properties

W. M. Shafer, Plastic Metals Div., National-U. S. Radiator Corp., Johnstown, Pa.

Electrolytic iron powder is produced commercially today by one United States and several foreign firms. The powder is produced by grinding and annealing brittle cathode deposits obtained usually from iron sulfate baths. The high purity and softness of this powder make it possible to fabricate powder metallurgy parts from it superior in properties to parts fabricated from less pure nonelectrolytic iron powder. A few applications are found in the chemical, pharmaceutical, and electronic fields.

Abstract No. 77

Electrolytic Iron Powder from a Caustic Bath

Adrien Le Duc, Diamond Alkali Co., P. O. Box 348, Painesville, Ohio, and **Luther Vaaler,** Battelle Memorial Institute, Columbus 1, Ohio

Conditions for electrodepositing iron powder from a slurry of iron III oxide in caustic solution were investigated. A ductile, dendritic deposit was obtained that could be ground up easily. The size of the dendrites was greatly influenced by conditions of deposition. Particle size distribution, particle shape, ductility, flowability, purity, and compactability of several powders were examined. Tensile strength and elongation of sintered compacts were also studied.

Abstract No. 78

Electrolytic Copper Powder—Production and Properties

E. J. Clugston and **Frank Wills,** American Metal Co., Ltd., 400 Middlesex Ave., Carteret, N. J.

The effects of electrochemical and mechanical variables on the physical characteristics of electrodeposited copper powder are reviewed. A description of the operation, equipment, and quality control facilities for the commercial production of electrolytic copper powder at the U. S. Metals Refining Co. is presented. In addition, the supporting research facilities are also described.

ELECTRO-ORGANIC

Abstract No. 79

Glow-Discharge Electrolysis in Aqueous Solutions

A. R. Denaro and **A. Hickling,** Dept. of Physical Chemistry, University of Liverpool, Liverpool, England

An investigation has been carried out of the reactions occurring when an electric discharge is passed from a positive electrode to the surface of an aqueous electrolyte containing oxidizable substrates such as ferrous, azide, ferrocyanide, and cerous ions. Electrolysis is accompanied by oxidation arising from the break-up of water molecules due to the bombardment of the solution by gaseous ions, and the chemical phenomena are analogous to the effects produced by ionizing radiations. An attempt has been made to develop a general mechanism of the process which will account quantitatively for the oxidation yields and their dependence on experimental conditions.

Abstract No. 80

Electrolytic Reduction of Cyanamide II. Nature of the Reduction of Cyanamide and Formamidine

Keijiro Odo, Eiichi Ichikawa, Katsujiro Shimogai, and **Kiichiro Sugino,** Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, Japan

Reduction of cyanamide to formamidine seemed to be of a catalytic nature; it took place smoothly at Pd black, Sn, or Cu rather than Pb or Hg. The fact that no wave of cyanamide was detected polarographically, although it was reduced macro-electrolytically, accounted for this observation. On the other hand, the reduction of formamidine might be electrochemical and could be made to proceed well at cathodes having high H overvoltage. In the latter, Hg gave very different products from those at other cathodes.

Abstract No. 81

Electrolytic Reduction of Organic Compounds, VII. Furfural

D. D. Staker and **C. L. Wilson,** Hudson Foam Plastics Corp., Lake Ave. and Saw Mill River Rd., Yonkers, N. Y.

Albert and Lowy reduced furfural at a Pb cathode in a medium of pH 4.5-6.5 and obtained furfuryl alcohol, the two stereoisomeric pinacols, and a resinous material which was not characterized. They showed that the resinous material was produced by the cathodic process and not by purely chemical changes occurring at the same time.

This work has been repeated and extended and an emphasis has been placed on the determination of the composition of the components of the resin. It seems to consist essentially of dimeric, trimeric, and tetrameric molecules. The dimeric component is isomeric with the pinacol, has the furan rings linked in the 2- and/or 5-positions, but does not possess hydroxyl groups on adjacent carbon atoms. The more complex components seem to have furan rings linked in a similar way and to have one hydroxyl group to each furan ring, but a large proportion of the material has hydroxyl groups on adjacent carbon atoms. The evidence obtained supports the view that the resinous products are formed as the result of 1,6-reduction of furfural.

Abstract No. 82

Electrolytic Reduction of Organic Compounds, VIII. Acetone

G. W. Mansel and **C. L. Wilson,** Hudson Foam Plastics Corp., Lake Ave. and Saw Mill River Rd., Yonkers, N. Y.

The reduction of acetone in alkaline solution has been extended with special reference to the effect of cation (Na, K, and NMe_4), concentration of acetone and electrolyte, temperature, current density, and effect of high speed rotation of the cathode. Most of the work was carried out using an amalgamated Cu cathode. Pinacol was determined by periodate titration. Current efficiencies were always over 90%. Reduction was carried out to not more than 15% and the products were entirely pinacol and alcohol.

Improvement in the yield of pinacol results from increased acetone concentration and lowered temperature in electrolytes. Increasing current density increases pinacol with KOH, leaves it essentially unchanged with NaOH, and decreases it with NMe_4OH.

Rotation of the cathode increases the yield of pinacol but only at low temperatures and low acetone concentrations. Under these conditions the following figures have been obtained:

	NaOH	26	KOH	36	NMe_4OH	46
Stationary Cu/Hg						
Rotating Cu/Hg		35		44		53
Stationary Hg		6		30		53% pinacol

Abstract No. 83

An Electrolytic Study of the Course of the Clemmensen Reduction

R. A. Strehlow (present address: Oak Ridge National Lab., Oak Ridge, Tenn.) and **Sherlock Swann, Jr.**, University of Illinois, Urbana, Ill.

The electroreduction of 2-pentanone to n-pentane was carried out at a series of cathodes in the zinc-mercury alloy system. Yields of the hydrocarbon showed a distinct relation to the phase diagram of the alloy system when they were considered as functions of the cathode composition. Although amalgamated zinc is generally used as part of the reducing couple in the Clemmensen reduction of ketones to hydrocarbons, it was found that a zinc cathode afforded the best yield of hydrocarbon in the electrolytic reduction.

Abstract No. 84

Application of Electrodialysis to Halide Interconversion in Quarternary Salts

M. J. Allen and **J. Ocampo**, CIBA Pharmaceutical Products, Inc., Summit, N. J.

In many instances it is difficult to prepare directly a quaternary salt having the desired halide component by interaction of the amine and the alkyl or aryl halide. This is especially so in cases where the chloride salt is required. Therefore, the amine must first be reacted with an iodo or bromo quaternizing agent and then exchanged for the chlorine by chemical means. This exchange has been found to be accomplished more readily by electrodialysis of the quaternary salt, followed by addition of halogen to the catholyte with subsequent isolation of the new quaternary salt. In general with this technique it is possible to exchange any halide for another or prepare non-halogen-type salts.

Abstract No. 85

Electrochemical Reduction of the C_4 Dibasic Acids and Their Esters: Acetylenedicarboxylic, Dibromomaleic, and Dibromofumaric. Nature of the Products and Reaction Mechanisms

P. J. Elving, Dept. of Chemistry, University of Michigan, Ann Arbor, Mich., **Isadore Rosenthal**, Rohm and Haas Co., 5000 Richmond St., Philadelphia, Pa., and **J. R. Hayes** and **A. J. Martin**, Pennsylvania State University, University Park, Pa.

Acetylenedicarboxylic acid (ADCA), dibromomaleic acid (DBMA), and dibromofumaric acid (DBFA) have been reduced over a range of pH at a micro mercury dropping electrode, and at a massive stirred mercury cathode; coulometric measurements were made using the massive electrode. Reduction products were identified polarographically, and by isolation. DBFA and DBMA are quantitatively reduced to ADCA in a two-electron process. Between pH 0.4 and 3.0 ADCA is reduced in a three-electron process to form racemic-α, α'-dimethylsuccinic acid; the decarboxylation and dimerization process is explained by a free radical mechanism. The esters of the three acids react similarly, except for the diethyl ester of ADCA which is reduced to diethyl fumarate. The pH-dependency of half-wave potential values in acidic solution is discussed.

Abstract No. 86

Solid Electrode Voltammetry of Organic Compounds

Theodore Kuwana, T. R. Mueller, and **R. N. Adams**, Dept. of Chemistry, University of Kansas, Lawrence, Kans.

Solid electrode voltammetry has long remained a neglected area in polarographic research. Voltammetry at controlled current is especially adaptable to solid electrode systems. The application of two controlled current techniques to anodic oxidations at Pt electrodes is discussed. Both of these methods, current-scanning polarography and chronopotentiometry, yield valuable physicochemical information on organic molecules in addition to providing rapid and precise analysis. In many cases, this data cannot be obtained by conventional polarographic methods.

Abstract No. 87

Electrochemical Studies in Cyclic Carbonate Esters

C. W. Tobias, Dept. of Chemistry and Chemical Engrg., University of California, Berkeley 4, Calif.

Solubility and conductivity studies of solutions of inorganic salts in propylene carbonate, ethylene carbonate, and γ-butyrolactone show that these solvents, although not displaying great solvent power, possess many of the properties desirable for an easily handled nonaqueous ionizing medium. Electrodeposition trials indicate the range of metals which may be deposited in these media.

Abstract No. 88

Polarographic Studies in Dimethylformamide, IV. Behavior of Aldehydes and Ketones

S. Wawzonek and **A. A. Gundersen**, Dept. of Chemistry, State University of Iowa, Iowa City, Iowa

The polarographic behavior of benzophenone, acetophenone, and benzaldehyde has been studied in anhydrous dimethylformamide as a solvent with tetrabutylammonium iodide as the supporting electrolyte. Benzophenone gave two waves which indicated a stepwise reduction to benzohydrol. Large scale electrolysis confirmed this mechanism. The formation of the intermediate ketyl was demonstrated by the products isolated when the electrolysis was carried out in the presence of carbon dioxide and ethyl iodide. The former gave benzilic acid and the latter diphenylethylcarbinol.

Acetophenone, which gave one polarographic wave, formed acetophenone pinacol when electrolyzed on a large scale. The intermediate ketyl apparently is unstable since only small amounts of atrolactic acid were formed in a large scale electrolysis in the presence of carbon dioxide. Benzaldehyde when reduced in a similar manner gave a poor yield of hydrobenzoin.

Abstract No. 89

Polarographic Reduction of Some Acetylenic Linkages

A. H. Gropp and **J. C. Ramsey, Jr.**, Dept. of Chemistry, University of Florida, Gainesville, Fla.

Two series of unsaturated quaternary ammonium salts were prepared, each compound containing an acetylenic linkage. In one series the unsaturated group was held constant and the saturated groups varied; in the other series the saturated groups were held constant and the unsaturated group lengthened. It was found that increasing the size of the saturated groups lowered the polarographic reduction potential, while lengthening the unsaturated group increased the reduction potential.

Abstract No. 90

Polarographic Reduction of Some Nitrofluorenones

Julia Gary, R. M. Powers, and **R. A. Day, Jr.**, Dept of Chemistry, Emory University, Emory University, Ga.

The polarographic reduction of 2-nitro, 2,5-dinitro, and 2,7-dinitrofluorenone has been studied in acetone-water media at various pH values. Attempts to interpret the reactions responsible for the various waves are reported. Coulometric measurements of the number of electrons consumed in different stages of reduction have been made. Evidence regarding the stability of the 9-fluoryl free radical is discussed.

Abstract No. 91

Electrochemical Reduction of Some Nitramines and Nitrosamines, I. Polarographic Behavior of Some Alkyl and Aryl Nitrosamines

G. C. Whitnack, R. D. Weaver, and **H. W. Kruse**, Chemistry Div., Research Dept., U. S. Naval Ordnance Test Station, China Lake, Calif.

The general behavior of dimethyl-, diethyl-, dipropyl-, diisopropyl-, and diphenylnitrosamine was investigated at the dropping mercury electrode. The effect of pH on the reduction process was studied in well-buffered media. Well-defined waves were produced for all the nitrosamines in 20% ethyl alcohol solutions of both mineral and organic acids. Presence of the dialkylhydrazines as the main reduction products was demonstrated by large-scale electrolysis.

Abstract No. 92

A Polarographic Study of Sodium-iodomethane Sulfonate in Various Media

M. J. Allen and **V. J. Powell**, Research Dept., CIBA Pharmaceutical Products, Inc., Summit N. J.

Studies were performed using three different media: pH 3.6 and 9.18, Clark and Lubs buffers, and 0.1*N* KNO_3. Concentrations of sodium-iodomethane sulfonate varied from 0.5×10^{-4} to 3.5×10^{-3}M. In all media there was a linear correlation between id and concentration. In the buffered media there was an appar-

ent one-electron change indicative of the following reaction:

$$2\,I\,CH_2SO_3^- + 2e$$

$$+ 2H \rightarrow \begin{vmatrix} CH_2SO_3^- \\ \\ CH_2SO_3^- \end{vmatrix} + 2\,HI$$

In the neutral medium (0.1*N* KNO_3) at the lower concentration the molecule appeared to undergo a one-electron change. As the concentration of depolarizer increased the reaction approached a two-electron change which indicated the formation of methane sulfonate:

$$I\,CH_2SO_3^- + 2e + 2H \rightarrow CH_3SO_3^- + HI$$

Abstract No. 93

Polarographic Behavior of Iodinated X-Ray Contrast Agents

Peter Kabasakalian, Schering Corp., Bloomfield, N. J.

Ten iodine-containing x-ray contrast compounds have been studied polarographically in 50% aqueous ethanol solutions at various *p*H values between 1.3 and 10.5. Both the qualitative behavior (change in wave form and positions with *p*H) and the quantitative behavior (change in wave magnitude with changes in sample concentration and temperature) of these compounds have been determined. Some macro scale electrolyses have been carried out at a mercury pool electrode to establish the degradation order of a few of these compounds.

Abstract No. 94

Polarography of Organo Tin Halides

C. M. Wheeler, Jr., Dept. of Chemistry, University of New Hampshire, Durham, N. H.

The polarographic characteristics of phenyl and alkyl substituted tin halides are presented. A well-defined reduction wave for tin is observed when organo-tin halides are reduced polarographically in dimethylformamide solvent. Increased phenyl substitution shifts the half-wave potential to a more negative value. Short chain alkyl substitution renders the tin more difficult to reduce than does similar phenyl substitution. The particular halide anion used contributes a small but significant effect on the half-wave potential.

Abstract No. 95

Polarographic Behavior of Steroids

Peter Kabasakalian, Schering Corp., Bloomfield, N. J.

The polarographic reduction waves of several $\Delta^{1,4}$-3-ketosteroids and Δ^4-3-ketosteroids have been studied at various pH values in 50% ethanol-water solutions buffered with organic buffers. Changes in magnitude and position of the wave as effected by changes in pH, concentration of steroid, temperature, and mercury pressure are recorded and discussed. A possible electrode reaction mechanism has been proposed on the basis of results obtained from wave analyses and diffusion coefficient determinations. Preliminary studies of controlled potential electrolysis products support the proposed mechanism.

Abstract No. 96

Correlation of Polarographic Half-Wave Potentials with Nuclear Magnetic Resonance 'Chemical Shifts'

C. E. Bennett, (present address: Polychemicals Dept., E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.) Aeronautical Research Lab., Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, and **P. J. Elving,** Dept. of Chemistry, University of Michigan, Ann Arbor, Mich.

The extent to which polarographic half-wave potentials of organic compounds can be correlated with nuclear magnetic resonance "chemical shifts" is discussed. A linear relationship between the two parameters was obtained for formaldehyde, acetaldehyde and propionaldehyde, and for meta- and parasubstituted benzaldehydes, iodobenzenes, and nitrobenzenes. Nonlinear results were obtained for ortho-substituted compounds and for a variety of reducible aliphatic compounds. These data support the generally accepted view that changes in half-wave potentials with structure are due both to electronic and steric effects.

Abstract No. 97

Correlation of Polarographic Half-Wave Potentials of Organic Compounds

P. J. Elving, Dept. of Chemistry, University of Michigan, Ann Arbor, Mich., and **C. E. Bennett** (present address: Polychemicals Dept., E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.) Aeronautical Research Lab., Wright Air Development Center, Wright-Patterson Air Force Base, Ohio

A generalization for correlating polarographic half-wave potentials of organic compounds with both structural and environmental factors is proposed. In a given type of molecule, the reduction of an electroactive group is facilitated as the electron density is decreased about the atom which will be attacked by an electron or electrons from the cathode. This decrease in electron density may be accomplished by many factors, e.g., substitution, orientation (adsorption) of the molecule at the electrode, *p*H, solvent, background electrolyte, etc. The validity of this concept is examined in respect to several representative factors including a discussion of the significance of half-wave potentials for irreversible processes. Previous correlations of half-wave potential with other experimental and theoretical approaches are reviewed.

ELECTROTHERMICS AND METALLURGY

Abstract No. 98

Equilibria between Titanium Metal and Solutions of Titanium Dichloride in Fused Sodium Chloride

K. Komarek and **P. Herasymenko,** Metallurgical Engrg., Research Div., New York University, New York 53, N. Y.

Thermal analyses of $TiCl_2$ and NaCl in closed Ti metal crucibles were made in the range from 0 to 100 wt % $TiCl_2$. The titanium chloride present in the salt mixtures was practically all in the divalent form. The melting point of $TiCl_2$ was confirmed to be 1025°C. The phase diagram of the system $NaCl{\cdot}TiCl_2$ has two compounds and one eutectic. The eutectic point lies at about 50.0 wt % $TiCl_2$ and 605°C. One compound with the tentative formula $NaCl{\cdot}TiCl_2$ is formed by a peritectic reaction at 628°C, the other one—2 $NaCl{\cdot}TiCl_2$—decomposes in the solid state at 548°C.

Abstract No. 99

Reaction Kinetics of the Nitriding of Titanium Dioxide

D. L. Douglass, J. H. Borden, and **G. R. St. Pierre,** Dept. of Metallurgical Engrg., The Ohio State University, Columbus, Ohio

A study of the separation of Ti from ilmenite by the selective formation of TiN was initiated by reacting NH_3 with TiO_2 (unit activity of TiO_2) at 900°C. After an initial transition period of ½ hr, during which the reaction rate increased, $TiN_{0.42}$ formed by a pseudo first-order reaction. Upon complete disappearance of TiO_2, nitrogen was absorbed into the $TiN_{0.42}$ lattice until $TiN_{0.60}$ existed after 20 hr. $TiN_{1.0}$ was obtained within 20 hr at 1000°C. A tentative reaction mechanism is proposed.

Abstract No. 100

Continuous Electrolytic Process for the Production of High Purity Beryllium Metal

S. J. Morana, The Beryllium Corp., Reading, Pa.

An improved, continuous electrolytic process for the production of high purity beryllium metal using a low temperature fused salt bath consisting of beryllium chloride and sodium chloride is described. The evolutionary steps involved are summarized. The continuous electrolysis unit consists of several cells in a common electrolyte. Improvements for removal of electrolyte from metal dendrites, lining the cathodes to improve purity, acid treating the final product, etc., are given.

Abstract No. 101

Equilibrium Reduction of Tungsten Oxides by Hydrogen

R. C. Griffis, Refractory Metals Lab., General Electric Co., Cleveland 17, Ohio

A study has been made on the heterogeneous equilibrium involving H_2-W-WO_2-H_2O, in the temperature interval 500°-1000°C. The apparatus constructed for equilibrium experiments and the method of synthesis of all the pure oxide phases of samples and x-ray standards are described in detail. The equilibrium data for this system have been treated by "Sigma" functions to obtain $\Delta F°$ and $\Delta H°$, for the formation of WO_2 from the elements, as a function of temperature. Difficulties arising during the study of the higher oxide systems is discussed.

Abstract No. 102

A Review of the Uses and Markets for Ferroalloys

R. W. Hale, Industrial Economics Div., Battelle Memorial Institute, Columbus 1, Ohio

A brief discussion is given concerning the structure of the industry, production and consumption of ferroalloys, uses of ferroalloys, trends in these uses, and the future growth of the industry. Sources of raw materials and such influencing factors as transportation, power availability, and location of markets are considered.

Abstract No. 103

Metallurgical Design of Submerged Arc Furnaces

W. M. Kelly, Electro Metallurgical Co., P. O. Box 580, Niagara Falls, N. Y.

Design of submerged arc furnaces has been largely a matter of electrical circuit design and arbitrary electrode arrangements without sufficient regard to metallurgical requirements. The present paper attempts to provide a basis for designing into the furnace the necessary electrical and dimensional relationships for good metallurgical results on specific smelting applications.

Basic electrical conditions for the major ferroalloy products are presented as a design foundation. Subsequent dimensional relations involving electrode size and spacing, reaction zone sizes, and furnace shell depth and diameter are discussed. Dimensional relations when comparing packet type vs. round type of submerged arc furnaces are included.

Abstract No. 104

Electric Smelting of Low Grade Nickel Ores

L. H. Banning, Bureau of Mines, U. S. Dept. of the Interior, Albany, Oreg.

During the past several years, the U. S. Bureau of Mines has conducted electric smelting investigations on several oxidized low grade nickel ores at its Northwest Electrodevelopment Experiment Station, at Albany, Oreg. The tests have been made on ores from Riddle and Gold Beach, Oreg., Cle Elum, Wash., and on foreign ores from Brazil, Cuba, and the Philippine Islands. The ores contain from 0.7 to 4.4% Ni. Low carbon ferronickel products containing from 2.3 to 50% Ni were produced. Results of these tests are summarized and evaluated. The smelting method and uses for the ferronickel product are discussed.

Abstract No. 105

Dissociation and Electrical Conductivity of Molten Silicates

Axel Wejnarth, 97 Hamilton Blvd., Kenmore 17, N. Y.

The electronic conductivity in silicates, when measuring their combined electronic and electrolytic conductivity, is eliminated when measuring the capacitance of the silicates in correlation to existing electrolytic polarization. A large polarization capacity in the measuring equipment makes a direct proportionate measurement of existing dissociation possible.

Abstract No. 106

Ferroalloys from Low Grade Ores by the Udy Processes

M. C. Udy and **M. J. Udy,** Strategic-Udy Metallurgical & Chemical Processes, Ltd., Niagara Falls, Ont.

A two-step electric arc furnace process selectively removes iron from low grade ores in a first step and then produces standard ferroalloys in a final step. A combination of furnace design, furnace operation, and slag control makes this process feasible with low grade, low cost ores. Prototype plant operation has already demonstrated production of standard grade ferromanganese from ores containing 11% Mn and 16% Fe. The process is even more attractive with higher grade ores.

Abstract No. 107

Experimental Production of Iron, Silicospiegeleisen, and Portland Cement from a Low Grade Manganiferous Iron Ore

R. A. Campbell, G. N. Banks, and **R. R. Rogers,** Mines Branch, Div. of Mineral Dressing and Process Metallurgy, Dept. of Mines and Technical Surveys, 552 Booth St., Ottawa, Canada

The ore, containing Fe 30%, Mn 4%, and SiO_2 50%, was treated experimentally by a two-stage smelting process in a 250 kva furnace to produce iron, silicospiegeleisen, and slag. The slag was mixed with limestone and calcined to produce a clinker which, on grinding, had the analysis and properties of portland cement. About 35 tons of ore were processed. The two smelting stages required 11 and 7 days, respectively.

Abstract No. 108

Small, Single-Phase, Dry-Top Electric Furnace for Experimental Smelting of Manganese Ores

D. D. Blue, U. S. Dept. of the Interior, Bureau of Mines, Region II, 500 Dale St., Boulder City, Nev.

As a part of its manganese program the Bureau of Mines has conducted smelting tests for the production of standard ferromanganese from various concentrates and off-grade ore. This paper describes the various single-phase furnaces used and the furnace as finally developed and standardized against commercial practice to obtain comparative data.

Abstract No. 109

Electrodeposition of High Purity Chromium

F. E. Block, P. C. Good, and **G. Asai,** Bureau of Mines, U. S. Dept. of the Interior, Albany, Oreg.

Thick Cr deposits were prepared by the electrolysis of aqueous chromic acid baths. Metal containing 0.005% oxygen, less than 0.002% nitrogen, and only traces of metallic impurities was obtained on electrolysis of purified solutions at elevated temperatures. After consumable electrode arc-melting, Cr could be hot worked to rod and drawn to wire which was ductile at room temperature.

SPRING MEETING

at the

STATLER HOTEL

New York, N. Y.

April 27, 28, 29, 30, and May 1, 1958

Sessions probably will be scheduled on

Electric Insulation
Electronics (including Luminescence, Semiconductors, Oxide Cathodes, Instrumentation, and possibly Screen Applications)

Electrothermics and Metallurgy
Industrial Electrolytics
Theoretical Electrochemistry

Abstracts for the Spring Meeting *(not exceeding 75 words in length)* must reach the Secretary's Office, 1860 Broadway, New York 23, N. Y. *not later than January 2, 1958* in order to be included in the program.

Indicate on abstract for which Division's symposium the paper is to be scheduled.

INDEX TO AUTHORS

(The number in the right hand column is the abstract number used in the Technical Program and in the Abstracts.)

	Abstract No.
Adams, G. B., Jr.	46
Adams, R. N.	86
Albrecht, W. M.	47
Allen, M. J.	84, 92
Alpert, M. B.	71
Andrew, K. F.	48
Apel, Charles	31
Asai, G.	109
Bakish, Robert	51
Banerjee, B. C.	68
Banks, G. N.	107
Banning, L. H.	104
Beck, A. F.	42
Bennett, C. E.	96, 97
Bennett, R. E.	47
Block, F. E.	109
Blue, D. D.	108
Borden, J. H.	99
Boswell, T. L.	21
Bothwell, M. R.	35, 36
Brodd, R. J.	14
Brown, M. H.	37, 38
Brown, R. H.	37, 38
Buob, K. H.	42
Burbank, Jeanne	1
Butler, T. J.	41
Campbell, R. A.	107
Carlin, F. X.	60
Clark, W. E.	44
Clugston, E. J.	78
Cohen, M.	34, 42
Cook, E. H.	38
Cutler, L. H.	28
Day, R. A., Jr.	90
Dean, R. S.	70
Denaro, A. R.	79
Dereska, Joseph	58
Dittmann, J. E.	5
Douglass, D. L.	99
Ellis, G. B.	10
Elving, P. J.	85, 96, 97
Fleischer, Arthur	10, 11
Frant, M. S.	63
Freund, J. M.	19
Gary, Julia	90
Gatos, H. C.	29
Geneidy, Ahmad	69
Gibbs, D. S.	32
Gleason, H. S.	19
Glicksman, R.	24, 25, 26, 27
Goldberg, M. B.	20
Good, P. C.	109
Gropp, A. H.	89
Goswami, A.	68
Griffis, R. C.	101
Gulbransen, E. A.	48
Gullett, W. W.	70
Gundersen, A. A.	88
Hale, R. W.	102
Harvey, W. W.	29
Hayes, J. R.	85
Herasymenko, P.	98
Hickling, A.	79
Hoey, G. R.	34
Hovorka, Frank	58
Huttly, M.	73
Ichikawa, Eiichi	80
Jenny, A. L.	50
Jensen, P. E.	3, 4
Jones, E. L.	8, 12
Kabasakalian, Peter	93, 95
Kass, S.	49
Katz, H. L.	64
Kelly, W. M.	103
Kirk, R. C.	18
Knapp, B. B.	57
Koehler, W. A.	69
Komarek, K.	98
Kozawa, Akiya	15, 16
Kruger, Jerome	30
Kruse, H. W.	91
Kuwana, Theodore	86
Lander, J. J.	6
Le Duc, Adrien	77
Lee, T. S.	46
Levy, Charles	59
Lincoln, John, Jr.	43
Lowenheim, F. A.	60
Lozier, G. S.	28
Machu, Willi	69
MacNamara, E. L.	61
Magari, Saburo	67
Mallett, M. W.	47
Mansel, G. W.	82
Mantell, C. L.	75
Martin, A. J.	85
McCawley, F. X.	70
McGraw, L. D.	23
McKay, R. J.	57
Meyers, W. F.	19
Minford, J. D.	37, 38
Minnick, L. J.	19
Morana, S. J.	100
Morehouse, C. K.	24, 25, 26, 27, 28
Mueller, T. R.	86
Nagley, F. R.	64
Ocampo, J.	84
Odo, Keijiro	80
Okada, Shinzo	67
Orem, T. H.	66
Ovenston, T. C. J.	65
Parker, C. A.	65
Pemsler, J. P.	45
Powers, R. M.	90
Powell, V. J.	92
Pribble, M. J.	15
Procter, K. L.	64
Ramsey, J. C., Jr.	89
Read, H. J.	56, 72
Reed, H. B., Jr.	20
Ritchie, E. J.	3, 4
Robinson, A. E.	65
Rockey, R. E.	10
Rogers, R. R.	107
Roll, K. H.	74
Rosenthal, Isadore	85
Rowan, W.	62
Ruetschi, Paul	2
Ruscetta, R. A.	50
St. Pierre, G. R.	99
Sam, Ahmed	15
Sams, J. F.	5
Sasaki, Kumazo	17
Schultz, F. J.	71
Sellers, W. W.	60
Shafer, W. M.	76
Shimogai, Katsujiro	80
Shotwell, J. J.	18
Simon, A. C.	8, 12
Skwirzynski, J. K.	73
Stadelmaier, H. H.	39
Staker, D. D.	81
Stern, Milton	33
Stoertz, H.	7
Strauss, H. J.	9
Strehlow, R. A.	83
Sugino, Kiichiro	80
Sullivan, W. F.	71
Svec, H. J.	31, 32
Swann, Sherlock, Jr.	83
Thomas, D. E.	49
Tobias, C. W.	87
Tripler, A. B., Jr.	23
Udy, M. C.	106
Udy, M. J.	106
Uhlig, H. H.	43
Vaaler, Luther	77
Van Rysselberghe, Pierre	46
Vermilyea, D. A.	52, 53, 54, 55
Vincent, G. D.	13
Vosburgh, W. C.	15, 16
Wawzonek, S.	88
Weaver, R. D.	91
Weininger, J. L.	22, 40
Wejnarth, Axel	105
Whalen, T. J.	72
Wheeler, G. M., Jr.	94
Whitener, E. M.	39
Whitnack, G. C.	91
Wills, Frank	78
Wilson, C. L.	81, 82
Yeager, Ernest	58

Current Affairs

Candidates for Society Offices–1958-1959

Sherlock Swann, Jr.

H. B. Linford

H. M. Scholberg

Ernest Yeager

The Nominating Committee, C. L. Faust, A. E. Middleton, A. U. Seybolt, U. B. Thomas, and H. H. Uhlig, Chairman, appointed by President Norman Hackerman, having met at Washington, D. C., during the 111th Meeting of The Electrochemical Society, presents the following list of candidates for office for the term 1958-1959:

For President—
Sherlock Swann, Jr.

For Third Vice-President—
Henry B. Linford
Harold M. Scholberg
Ernest Yeager

For Treasurer (three-year term)—
Lyle I. Gilbertson

These candidates have been notified, and each has expressed his willingness to run for office and to serve if elected.

The two other Vice-Presidents, W. C. Gardiner and R. A. Schaefer, since they were elected for a three-year term, will automatically become first and second Vice-President, respectively.

The above slate will be voted on in the fall ballot-by-mail election—the successful candidates to assume office in the spring of 1958.

Sherlock Swann Jr.

Presidential Candidate

Sherlock Swann, Jr., is currently Divisional Editor of the JOURNAL for the Electro-Organic Division, and is serving on the Ways and Means and Perkin Medal Committees.

During his membership in the Society, which began in 1928, Dr. Swann has held many offices and devoted much time to the various interests of the Society. Included in the offices he held are: Manager from 1934 to 1940; Vice-President from 1941 to 1943; and again Manager from 1943 to 1946. He has also been prominent in the Electro-Organic Division of the Society, of which he was Secretary-Treasurer from 1940 to 1942; Vice-Chairman, 1942 to 1944; and Chairman from 1944 to 1946; and has served on many committees. During the past year he was Chairman of the Ways and Means Committee.

Dr. Swann was born in Baltimore, Md., and received his B.S. degree from Princeton University in 1922, and his Ph. D. degree in organic chemistry from The Johns Hopkins University in 1926. The following year he became a member of the Division of Chemical Engineering, Engineering Experiment Station, University of Illinois, and has been Research Professor of Chemical Engineering at that university since 1941. His principal research is in the field of electro-organic chemistry. He is the author of a number of papers in the TRANSACTIONS and JOURNAL of the Society, of a chapter in "Technique of Organic Chemistry. Vol. II: Catalytic, Photochemical, and Electrolytic Reactions," second edition, edited by Arnold Weissberger, Interscience Publishers, New York (1948), and articles on electro-organic chemistry in "Encyclopedia of Chemical Technology", Vol. 5, edited by Raymond E. Kirk and Donald F. Othmer, Interscience Encyclopedia Inc., New York (1950), and in "The Encyclopedia of Chemistry," edited by George L. Clark, Gessner G. Hawley, and William A. Hamor, Reinhold, New York (1957).

Henry B. Linford

Vice-Presidential Candidate

Henry B. Linford, Professor of Chemical Engineering, Columbia University, was born in Logan, Utah, in 1911. He received his undergraduate training at Utah State University and his graduate training at the State College of Washington, receiving the Ph.D. degree in physical chemistry in 1936. In 1936 he was awarded the Weston Fellowship by The Electrochemical Society and worked under the direction of Dr. Colin G. Fink at Columbia University during the school year 1936-37. He then served as a Research Electrochemist at the American Smelting & Refining Company in New Jersey.

Dr. Linford joined the staff of Columbia University as an Instructor in 1941. He became an Assistant Professor in 1946, an Associate Professor in 1949, and a Professor in 1952. His research interests deal principally with the field of electrochemical engineering. He and his students have published numerous articles on preparation of metal surfaces for electroplating, on electroplating, and corrosion.

A member of The Electrochemical Society since 1935, Dr. Linford served as Chairman of the New York Section in 1943 and Chairman of the Corrosion Division in 1948, and has been the National Secretary since 1949. He belongs to the American Electroplaters' Society, of which he has been Director of Research Project No. 12 since 1949. He also holds memberships in Phi Lambda Upsilon, Sigma Xi, the American Institute of Chemical Engineers, the National Association of Corrosion Engineers, and is a Fellow in the New York Academy of Sciences.

Harold M. Scholberg

Vice-Presidential Candidate

Harold M. Scholberg, Research Associate in the Central Research Lab. of Minnesota Mining & Manufacturing Co., St. Paul, Minn., was born in Minot, N. D., July 6, 1910. He received his B.S. and M.S. degrees in chemical engineering from the University of North Dakota in 1932 and 1933, respectively. For the next five years, except for two during which he was a research chemist for the Hendricks Research Corp., he attended the University of Chicago, where he earned his Ph.D. degree in 1938 and where he met his wife, also a chemist, who completed two years of graduate work at Chicago.

From 1938 to 1941 Dr. Scholberg was a research chemist for Sherwin-Williams Paint Co. and from 1941 until 1944 with American Can Co. Joining Minnesota Mining & Manufacturing Co. in 1944, he became Section Leader in the Electro Fluorination Group in 1948, Assistant Director in 1951, Associate Director in 1953, and Research Associate in 1955. His publications and patents have been on surface chemistry and on the electrochemical fluorination of organic compounds. His interests at the present time are solid state physics.

Mr. Scholberg joined The Electrochemical Society in May 1948 and has served as Secretary, Vice-Chairman, and Chairman of the Organic Division. Currently, he is a member of the Acheson Award Committee. His other professional associations are the American Chemical Society, Sigma Xi, and the Chicago Chemists Club. While chairman of the publicity committee for the Minnesota Section of the American Chemical Society, he organized the first chemical TV series in the country. Mr. Scholberg's activities outside the chemical profession include the leadership of a Great Books discussion group, and Civil Defense.

Ernest Yeager

Vice-Presidential Candidate

Ernest Yeager, Associate Professor of Chemistry at Western Reserve University in Cleveland, Ohio, was born in Orange, N. J., in 1924. He received his B.A. from New Jersey State Teachers College and then pursued graduate work in chemistry at Western Reserve, from which he received his M.S. in 1946 and his Ph.D. in physical chemistry in 1948. From 1947 to 1948 he held a Coffin Fellowship from the General Electric Educational Fund. Since that time to the present he has been a member of the faculty of Western Reserve. In 1953 he was appointed Associate Professor of Chemistry.

Dr. Yeager's research interests include electrochemistry, ultrasonics, and emission spectroscopy. His publications in the field of electrochemistry are concerned with electrode kinetics as well as electrolytes and colloids. Several of his publications in the field of physical acoustics involve the use of ultrasonic techniques for the study of electrochemical systems. The research of Dr. Yeager and his graduate students in the field of spectroscopy has extended from the basic processes involved in the excitation of spectra to the trace analysis of metallic elements in cancerous tissue.

Dr. Yeager has participated actively in the affairs of the Society as Vice-Chairman and subsequently Chairman of the Theoretical Electrochemistry Division. He has served as a member of the Ways and Means Committee and is a past Chairman of the Cleveland Section of the Society.

In 1956 at the Second International Congress on Acoustics, Dr. Yeager was awarded the Biennial Award of the Acoustical Society of America, an award which is made once every two years to a person under 35 years of age for outstanding research in the field of acoustics. In 1954 he received the annual Technical Award of the Cleveland Technical Society Council.

At the present time Dr. Yeager is Chairman of the Committee on Physical Acoustics of the Acoustical Society of America and a fellow of that Society. He is a past president of the Cleveland Society on Spectroscopy.

Lyle I. Gilbertson

Candidate for Treasurer

Lyle I. Gilbertson, Director of the Murray Hill Laboratories of Air Reduction Company, Inc., Murray Hill, N. J., was born in 1903 near Beloit, Wis. A graduate in chemistry of Augustana College in 1925, he received the M.A. degree the following year from the University of Wisconsin and in 1940 the Ph.D. degree in inorganic chemistry from Indiana University.

After a year as instructor at Carleton College, Northfield, Minn., in 1926-1927, he became a member of the staff of the Department of Chemistry and Chemical Engineering of the State College of Washington, remaining there until 1942 when he joined the Division of War Research at Columbia University. Later he was affiliated with the Manhattan Project. In 1946 he joined the research staff of the Air Reduction Company.

Dr. Gilbertson's research activities have been largely in the field of inorganic chemistry. He also worked for a period of time on problems on the electrodeposition of silver; this work was begun at Indiana University as a student of Professor Frank C. Mathers. He has contributed papers on electrodeposition to the TRANSACTIONS of The Electrochemical Society and to other publications in the fields of selenium and tellurium chemistry.

As a member of The Electrochemical Society since 1935, Dr. Gilbertson's activities have included the chairmanship of the New York Metropolitan Section and, since 1950, the chairmanship of the Membership Committee and membership on the Admissions Committee. He is also a member of Phi Lambda Upsilon, Sigma Xi, Alpha Chi Sigma, the New York Academy of Sciences, American Institute of Chemists, and the American Chemical Society.

Section News

Boston Section

The seventh meeting of the Boston Section was held on May 6, 1957 at the M. I. T. Graduate House. The following officers were elected for the coming year:

Chairman—L. B. Rogers, M. I. T.

Vice-Chairman — Charles Levy, M. I. T.

Secretary-Treasurer—G. W. Waring, Raytheon Manufacturing Co., 55 Chapel St., Newton 58, Mass.

Representative on the Council of Local Sections—F. C. Benner (2 years), National Research Corp.

Mr. Lyle W. Evans, Sylvania Electric Products Inc., Seneca Falls, N. Y., presented a Ladies' Night paper on "Chemical Problems in Color Television Tube Manufacture." In the color TV tube, electrons are

driven to the screen by three guns rather than the one used in monochrome tubes. In the shadow mask tube, which is currently in production, it is necessary to apply three color screens separately to yield green, blue, or red, or any combination thereof. The individual screen is applied by coating the glass face with a "photoresist" and phosphor, then portions are exposed through the shadow mask, and developed with a water spray which washes off the unexposed areas and leaves behind a pattern of dots corresponding to the holes in the mask. In preparing the "photoresist," polyvinyl alcohol was found best to fit the requirements for the base material, and ammonium dichromate or potassium dichromate are more commonly used as sensitizers.

The phosphors must be carefully chosen for color and purity, brightness level, for the method of deposition with special attention to particle size and distribution and, finally, for stability during processing. The phosphors currently used in preparation of color TV tubes are zinc sulfide, zinc silicate, and zinc phosphate.

Methods of screen deposition include settling, spraying, slurry, and dusting. Each method has certain advantages in meeting the stringent requirements. The correct exposure is extremely important and dependent on the screen weight and texture, light source characteristics, mask characteristics, and, of course, time, temperature, and humidity.

A set of dots must have uniform phosphor weight, uniform diameter center to edge, uniform density and packing, in any of the three screens, in order to avoid a white field with varying degrees of color shading in those areas which are nonuniform. From the tube quality standpoint, this is probably the most important and hardest test to meet.

Charles Levy,
Vice-Chairman

Detroit Section

Officers of the Detroit Section for the coming year were elected at a recent meeting as follows:

Chairman—Manuel Ben, 13430 Rosemary Dr., Oak Park 37, Mich.

Vice-Chairman—Sam Piken, 2632 Lari Ct., R#1, Orchard Lake, Mich.

Second Vice-Chairman—A. E. Remick, Wayne University, Detroit, Mich.

Secretary-Treasurer — Manuel Shaw, Chrysler Corp., Engineering Div., Dept. 931, P. O. Box 1118, Detroit 31, Mich.

Representatives on the Council of Local Sections—Frank Passal and Lee O. Case.

Manuel Shaw,
Secretary-Treasurer

San Francisco Section

The following members have been elected officers of the San Francisco Section for the year 1957-58:

Chairman—H. F. Myers, Columbia-Geneva Steel Div., 120 Montgomery St., San Francisco 6, Calif.

Vice-Chairman—Bernard Porter, Kaiser-Aluminum & Chemical Corp., Reduction Group, Permanente, Calif.

Secretary—R. A. Zimmerly, Columbia-Geneva Steel Div., U. S. Steel Corp., Pittsburgh, Calif.

Treasurer—J. F. Aicher, E. A. Wilcox Co., 277 Seventh St., San Francisco 3, Calif.

Representatives on the Council of Local Sections—S. H. Dreisbach and C. D. Hunt.

R. A. Zimmerly,
Secretary

New Members

In June 1957 the following were approved for membership in The Electrochemical Society by the Admissions Committee:

Active Members

Robert S. Alwitt, Sprague Electric Co.; Mail add: 1010 State Rd., North Adams, Mass. (Industrial Electrolytic)

Armin O. Apelt, National Bureau of Standards; Mail add: 7512 Mendota Pl., Springfield, Va. (Battery)

Gerhard Barth-Wehrenalp, Pennsalt Chemicals Corp.; Mail add: P.O. Box 4388, Philadelphia 18, Pa. (Electric Insulation, Electrodeposition, Industrial Electrolytic, Theoretical Electrochemistry)

Leonard Bernstein, Hughes Aircraft Co.; Mail add: 819 N. Maertin Lane, Fullerton, Calif. (Electronics, Electrothermics & Metallurgy)

Thomas L. Boswell, Elgin National Watch Co.; Mail add: 22 N. Commonwealth, Elgin, Ill. (Battery, Electric Insulation)

By action of the Board of Directors of the Society, all prospective members must include first year's dues with their applications for membership.

Also, please note that, if sponsors sign the application form itself, processing can be expedited considerably.

Gilbert W. Castellan, The Catholic University of America, Dept. of Chemisty, Washington 17, D. C. (Theoretical Electrochemistry)

James E. Cline, Sylvania Electric Products Inc.; Mail add: 22 Beals St., Brookline 46, Mass. (Electronics)

John L. Dewey, Reynolds Metals Co., Reduction Research Lab., Sheffield, Ala. (Electrothermics & Metallurgy)

Carlyle S. Herrick, General Electric Co., Research Lab., Box 1088, Schenectady, N. Y. (Electronics)

Robert M. Hunter, General Electric Co., Columbia St., Clyde, N. Y. (Electronics)

Jacob M. Jost, Clevite Research Center; Mail add: 10817 Governor Ave., Cleveland 11, Ohio (Electronics)

William D. Klopp, Battelle Memorial Institute, 505 King Ave., Columbus 1, Ohio (Electrothermics & Metallurgy)

K. W. Leu, Koninklijke/Shell-Laboratorium, Badhuisweg 3, Amsterdam N., Holland (Corrosion, Electro-Organic, Electrothermics & Metallurgy)

Olof H. Lindberg, Westinghouse Electric Corp., 7325 Pennsylvania Ave., Pittsburgh 8, Pa. (Electronics)

Paula Lintz, Radio Corporation of America, Somerville, N. J. (Electronics)

Curtis J. McMinn, Reynolds Metals Co., Reduction Research Lab., Sheffield, Ala. (Industrial Electrolytic)

James E. Meinhard, National Cash Register Co.; Mail add: 26819 Westvale Rd., Rolling Hills, Calif. (Electronics, Theoretical Electrochemistry)

Frances Rosen, Hughes Aircraft Co.; Mail add: 6759 Yucca St., Hollywood 28, Calif. (Electronics, Theoretical Electrochemistry)

John W. Schell, Erie Resistor Corp.; Mail add: 5363 Cherry St., Erie, Pa. (Electronics)

William E. Schmidt, George Washington University; Mail add: 1324 Dale Dr., Silver Spring, Md. (Electrodeposition)

Raymond G. Seidensticker, Westinghouse Research Labs., Beulah Rd., Pittsburgh 35, Pa. (Electronics)

Willard B. Stone, Oxford Paper Co.; Mail add: 424 Penobscot St., Rumford, Me. (Industrial Electrolytic)

Alvin B. Topfer, Philco Corp.; Mail add: Welsh and Cedar Hill Rds., R.D. #1, Ambler, Pa. (Electronics)

Maurice L. Torti, Jr., National Research Corp., 70 Memorial Dr., Cambridge, Mass. (Electrothermics & Metallurgy)

Anselm Wachtel, Westinghouse Lamp Div.; Mail add: 101 Kendall Dr., Parlin, N. J. (Electronics)

Lincoln A. Warrell, Aluminum Co. of America, 744 Broad St., Newark 2, N. J. (Electronics)

Joseph L. Weininger, General Electric Co., Research Lab., P.O. Box 1088, Schenectady, N. Y. (Battery, Corrosion, Electronics, Theoretical Electrochemistry)

James E. Wells, III, Electro Metallurgical Co., Metals Research Labs.; Mail add: 211 Fourth St., Lewiston, N. Y. (Electrothermics & Metallurgy)

Associate Member

Marjorie J. Beebe, Sprague Electric Co., Marshall St., North Adams, Mass. (Electronics)

Transfer from Associate to Active Membership

Norman C. Craig, Harvard University; Mail add: 383 Harvard St., Apt. 111, Cambridge 38, Mass. (Theoretical Electrochemistry)

Deceased Reported During the Month of May, 1957

Karl F. Bonhoeffer, Busen Strasse, Gottingen, Germany

Louis Burgess, 233 Broadway, New York 7, N. Y.

Edward E. De Souza, Caixa Postal, 162, Sao Paulo, Brazil

Personals

James H. Schulman of the Naval Research Lab. was presented an Annual Science Award of the Naval Research Lab.'s Branch of the Scientific Research Society of America. Dr. Schulman, head of the Dielectrics Branch, received the society's Applied Science Award. Practical application of original discoveries in the field of luminescence mechanisms brought about the society's selection of Dr. Schulman for the award. His research led to the development of dosimeters, radiation measuring devices, which filled vital

(Continued on page 179C)

ECS Membership Statistics

The following three tables give breakdown of membership as of July 1, 1957. The Secretary's Office feels that a regular accounting of membership will be very stimulating to membership committee activities. In Table I it should be noted that the totals appearing in the right-hand column are *not* the sums of the figures in that line since members belong to more than one Division and, also, because Sustaining Members are not assigned to Divisions. But the totals listed are the total membership in each Section. In Table I, Sustaining Members have been credited to the various Sections.

Table I. *ECS Membership by Sections and Divisions*

Section	Division: Battery	Corrosion	Electric Insulation	Electro-deposition	Electronics	Electro-Organic	Electrothermics & Met.	Industrial Electrolytic	Theoretical Electrochem.	No Division	Total as of 7/1/57	Total as of 4/1/57	Net Change
Chicago	14	37	4	42	16	6	12	14	19	13	111	113	— 2
Cleveland	58	38	2	48	41	12	24	32	42	15	202	195	+ 7
Detroit	8	18	5	45	6	8	4	5	21	20	82	80	+ 2
India	7	5	1	15	4	5	6	13	7	3	31	27	+ 4
Midland	5	17	0	5	2	2	7	17	10	3	44	41	+ 3
New York	75	102	22	139	111	33	65	63	94	45	468	447	+ 21
Niagara Falls	11	23	0	20	3	5	73	59	22	23	164	156	+ 8
Pacific Northwest	5	15	0	11	1	1	5	11	8	10	47	47	0
Philadelphia	24	31	4	38	53	15	19	16	48	29	166	155	+ 11
Pittsburgh	4	47	3	28	26	5	33	16	35	10	130	117	+ 13
San Francisco	4	15	2	17	12	3	13	23	21	4	62	60	+ 2
Washington-Baltimore	32	42	8	39	22	3	10	11	29	7	124	117	+ 7
Ontario-Quebec	10	22	0	14	1	3	32	23	6	15	69	64	+ 5
U. S. Non-Section	49	92	12	92	57	38	51	75	108	37	383	486	—103
Boston	13	31	4	34	42	8	20	13	25	8	130	117	+ 13
Southern Calif.-Nev.	15	20	1	22	24	3	12	17	17	10	87	87	+ 16
Foreign Non-Section	39	55	6	61	27	27	36	58	67	55	216	212	+ 4
Mohawk-Hudson	5	14	15	9	12	1	7	3	9	6	52	0	+ 52
Columbus	1	12	0	13	5	3	20	2	8	6	44	0	+ 44
Indianapolis	10	7	4	8	9	4	5	2	6	2	36	0	+ 36
Total As of July 1	389	643	93	700	474	185	454	473	602	321		2648	
Total As of April 1	377	618	86	680	411	183	426	454	578	321	2505		

Table II. *ECS Membership by Grade*

	Total as of 7/1/57	Total as of 4/1/57	Net Change
Active	2355	2142	+213
Delinquent	73	146	— 73
Active Representative Patron Members	8	8	0
Active Representative Sustaining Members	62	60	+ 2
Total Active Members	2498	2356	+142
Life	15	15	0
Emeritus	46	44	+ 2
Associate	29	28	+ 1
Student	55	57	— 2
Honorary	5	5	0
	2648	2505	+143

The figures pertaining to Patron and Sustaining Member Representatives have been added to reflect reclassifications and changes in membership status.

Table III. *ECS Patron and Sustaining Membership*

	Total as of 7/1/57	Total as of 4/1/57	Net Change
Patron Member Companies	4	4	0
Sustaining Member Companies	121	119	+2

needs in three different fields: a military personnel dosimeter for nuclear radiation, a high level dosimeter for use in bomb tests and in food and drug processing, and a miniature dosimeter for medical use in body tissue.

Ira M. LeBaron has been elected vice-president in charge of research for International Minerals & Chemical Corp., Chicago. He will be in charge of the company's research

Ira M. LeBaron

and development program and will serve on the Research Committee. Previously, Dr. LeBaron had been director of research. He is the author of numerous research papers on subjects related to electrochemistry, inorganic chemistry, metallurgy, and ore dressings.

Albert Muller, until recently Director of Metallurgical Research at the Air Reduction Central Research Labs., Murray Hill, N. J., has been appointed Assistant to the President, Air Reduction Sales Co., a division of Air Reduction Co., Inc. In his new assignment he will assist the president of the division, Mr. J. H. Humberstone, with respect to the acquisition and the development of new products and processes. Dr. Muller is a specialist in the fields of ferrous and nonferrous process metallurgy, welding, and the development of high energy fuels and oxidants.

Joseph F. Donahue left the Naval Ordnance Labs. in May to become associated with Gould-National Batteries, Depew, N. Y.

S. Krishnamurthy has given up the post of Assistant Director (Chemicals), Indian Standards Institution, to assume the duties of Chief Chemist, Indian Telephone Industries (Private), Ltd., Bangalore District.

M. S. Thacker has been elected General President of the Forty-fifth Session of the Indian Science Congress to be held at Madras in January 1958.

S. Ramaswamy has been nominated a member of the Development Council for Heavy Chemicals (Alkalis), Government of India.

B. Narayan Das has been elected an Associate Member of the Institution of Engineers (India).

News Items

Young Author's Prize

At the Annual Banquet held on Tuesday evening, May 14, during the Washington Meeting of the Society, announcement was made of the award of the Young Author's Prize of $100 to Ralph S. Cooper, staff member in the Theoretical Division

R. S. Cooper

of the Los Alamos Scientific Lab. of the University of California. His prize-winning paper, "Anodic Transients of Copper in Hydrochloric Acid," prepared while he was a member of the Physics Dept. at the University of Illinois, Urbana, was published in the May 1956 issue of the JOURNAL.

After receiving his B.S. degree in chemical engineering from the Cooper Union, New York, in 1953, Dr. Cooper attended the University of Illinois, where he held a research assistantship in the Physics Dept. during the entire period of his graduate schooling. He received his M.S. in physics in 1954, his Ph.D. in physics in June 1957. Since March he has been at the Los Alamos Lab. In addition to The Electrochemical Society, he holds memberships in the American Physical Society, Tau Beta Pi, and Sigma Xi.

Turner Memorial Award

The Francis Mills Turner Memorial Award, sponsored by Reinhold Publishing Corp., consisting of $100 worth of books, was presented to J. H. Westbrook at the Annual Banquet of the Society, Tuesday evening, May 14, in Washington, D. C., for his paper "Temperature Dependence of Hardness of the Equi-Atomic Iron Group Aluminides," published in the January 1956 issue of the JOURNAL.

J. H. Westbrook

Dr. Westbrook was awarded his bachelor's and master's degrees in metallurgical engineering from Rensselaer Polytechnic Institute and received his Sc.D. from Massachusetts Institute of Technology in 1949. During 1946 and 1947 he was on the research staff of Rensselaer Polytechnic Institute. He joined the Research Lab. of the General Electric Co. in 1949 where he is now a member of the Ceramic Studies Section.

He has taught metallurgical courses at R.P.I. and M.I.T. and electronics for the U. S. Navy, while he was in the service. More recently he has given a course in metallurgy for the American Society for Metals.

He is the author of the Non-Ferrous Metals Section of the forthcoming sixth edition of Marks' "Handbook of Mechanical Engineering" and, with S. Mellgren, is translator of "Thermodynamics of Alloy Systems" by Wagner, published by Addison-Wesley in 1952.

Dr. Westbrook's research has been concerned with the mechanical properties of high temperature materials, metal-ceramic seals, thermal shock, hot pressing, resistance welding, synthesis and structure of intermetallic compounds, and most recently with hot hardness testing and temperature dependence of strength of high temperature materials. He has published numerous papers on these subjects both in the JOURNAL and elsewhere.

In addition to The Electrochemical Society he is a member of the American Institute of Mining and Metallurgical Engineers, the American Society for Metals, the American Ceramic Society, and the British Institute of Metals. He was recently

Manuscripts and Abstracts for Spring 1958 Meeting

Papers are now being solicited for the Spring 1958 Meeting of the Society, to be held at the Statler Hotel in New York City, April 27, 28, 29, 30, and May 1, 1958. Technical Sessions probably will be scheduled on Electric Insulation, Electronics, Electrothermics and Metallurgy, Industrial Electrolytics, and Theoretical Electrochemistry.

To be considered for this meeting, triplicate copies of abstracts *(not to exceed 75 words in length)* must be received at Society Headquarters, 1860 Broadway, New York 23, N. Y., *not later than January 2, 1958. Please indicate on abstract for which Division's symposium the paper is to be scheduled.* Complete manuscripts should be sent to the Managing Editor of the JOURNAL at 1860 Broadway, New York 23, N. Y.

* * *

The Fall 1958 Meeting will be held in Ottawa, Canada, September 28, 29, 30, October 1, and 2, 1958, at the Chateau Laurier.

elected Secretary-Treasurer of the Electrothermics and Metallurgy Division of the ECS.

Conference on Magnetism and Magnetic Materials

The American Institute of Electrical Engineers in cooperation with The American Physical Society, The American Institute of Mining and Metallurgical Engineers, The Institute of Radio Engineers, and the Office of Naval Research will sponsor a Conference on Magnetism and Magnetic Materials, Nov. 18-20, at the Hotel Sheraton-Park in Washington, D. C. For further information interested persons may write to the Local Conference Committee Chairman: L. R. Maxwell, U. S. Naval Ordnance Lab., Silver Spring, Md.

Aluminum Cable Manufacture in India

A new plant, the first of its kind in India to manufacture covered aluminum conductors, went into production in April 1957 at the Aluminum Industries Ltd., Kundara, Kerala State. It cost Rs. 5 lakhs, and is equipped for an annual output of three to five million yards of aluminum cable. This is a forerunner of many more ventures into the vast electrical industry area now monopolized by copper. In view of the copper shortage in India, the use of aluminum becomes very important. The aluminum cable produced by the plant is much lighter than the equivalent insulated copper cable and offers certain advantages in handling and installation. Another significant point is that the covered aluminum conductors could be made available at prices comparatively cheaper than those now ruling for insulated copper cable of equal rating.

Extraction Metallurgy Symposium

A symposium on "Mineral Beneficiation and Extractive Metallurgical Techniques" was organized by the National Metallurgical Lab., Jamshedpur, in February 1957. Among the 53 papers presented, the following are of electrochemical interest: resources and characteristics of Indian manganese ores with a view to their utilization for ferromanganese manufacture; processes of extraction of electrolytic manganese from low-grade ores developed in N.M.L.; application of physicochemical principles in extractive metallurgy; use of electric furnaces in the manufacture of metals; recovery of lead and antimony from battery waste; electrolytic extraction of zinc from low-grade ores.

Corrosion Metallurgy Symposium

A Symposium on "Corrosion of Metals" has been planned by the Section of Engineering and Metallurgy, Indian Science Congress, during the annual session of the Congress at Madras in January, 1958.

Book Review

The Surface Treatment and Finishing of Aluminium and Its Alloys by S. Wernick and R. Pinner. Published by Robert Draper Ltd., 85 Udney Park Road, Teddington, Middlesex, England, 1956. 580 pages + XVI, 187 figs., 105 tables. Price 84 s.—($12.00 U.S.A.) post free.

A new book written in English on the subject of the surface treatment and finishing of aluminum and its alloys is particularly welcome at this time when there is a marked increase in the use of aluminum in the structural field.

The introductory chapters of this book dealing with the properties of aluminum and the surface pretreatments such as buffing, etching, and brightening cover the subject in a satisfactory manner.

An extensive search of the literature has been made for the main chapters of the book dealing with conversion or chemical coatings, anodic coatings and plating with metal. Most of the important papers and patents dealing with the various subjects have been reviewed and abstracted. Excessive space has been devoted to various papers on the theory of anodic oxidation without critical editorial comment. Limited as the authors are to the patent and technical literature, they are not acquainted with some of the important details of the best commercial American finishing practices.

The subject matter dealing with dyeing and sealing of anodic coatings offers nothing particularly new but covers most of the best known and used procedures. The supposition that monohydrate is formed deep in the pores of sulfuric acid anodic coatings is still offered as the explanation of sealing.

The last three chapters of the book deal with organic finishing, vitreous enameling and metal spraying which are subjects not usually dealt with in a book on chemical and electrochemical finishing. These chapters are a welcome addition to the book.

The appearance of the book could have been improved by redrawing all the curves according to an established standard. Being a first edition there are the usual typographical errors and a few confusing and hard to understand paragraphs. The index is too abbreviated to be of much help in locating specific subjects.

While the book is not quite up to the high standard usually expected in a British text, the rather complete and up-to-date survey of the literature with excellent references makes this book a welcome addition to the English technical literature.

Ralph B. Mason

Meetings of Other Organizations

Sept. 8-13—American Chemical Society, National Meeting, New York, N. Y.

Sept. 15-18—American Institute of Chemical Engineers, Regional Meeting, Lord Baltimore Hotel, Baltimore, Md.

Oct. 1-4—National Association of Corrosion Engineers, North Central Regional Meeting, Chicago, Ill.

Oct. 1-4—National Association of Corrosion Engineers, South Central Regional Meeting, Oklahoma City, Okla.

Oct. 7-9—National Association of Corrosion Engineers Northeast Regional Meeting, Pittsburgh, Pa.

Nov. 13-15—American Standards Association, Annual Meeting and National Conference on Standards, St. Francis Hotel, San Francisco, Calif.

Announcements from Publishers

The Silver Oxide-Zinc Alkaline Primary Cell: Part 4, Anodic Characteristics of Zinc Alloys, C. M. Shepherd, Naval Research Lab., Feb. 1957. PB 121744,* 25 pages, 75 cents.

Chemical Surface Treatment of Titanium, H. A. Pray, P. D. Miller, and R. A. Jefferys, Battelle Memorial Institute for U.S. Army Ordnance Corps, May 1953. PB 111805,* 43 pages, $1.25.

Development of two chemical baths for coating the surfaces of titanium and its alloys for remarkable wear resistance is described.

The 1957 Isotope Index, "International Edition." Available at $3.00 each in the U.S. and Canada ($3.50 foreign); sent postpaid. Please send your remittance with your order. Order from Publications Dept., Scientific Equipment Co., 23 N. Hawthorne Lane, Indianapolis 19, Ind.

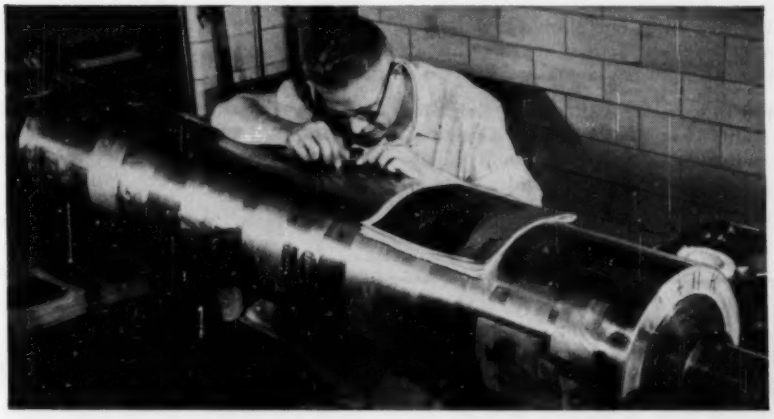
The second edition of this valuable guide to the isotopes is completely revised and expanded to 100 pages. Compiled from the latest suppliers' catalogs and from private communications The Isotope Index lists the source of every known commercially available isotope as of April 1, 1957. Included are both stable and radioactive isotopes and more than 700 labeled compounds of C-14, I-131, P-32, S-35, H-2, H-3, and many others. More than 3000 items in all (1500 for C-14 alone) from more than 50 U.S., Canadian, British, French, and German suppliers. Complete purchasing information is supplied including Chemical Name or Formula, Specific Activity, Supplier, Catalog Number, and Latest Prices. Also included for each isotope is its half-life and principal radiation energies. In addition, The Isotope Index includes sections on the available Calibration samples, Radiographic and Therapeutic Sources, a complete list of known suppliers, and a brief section on the revised A.E.C. requirements.

A Guide to the Literature of Chemistry, by E. J. Crane, Austin M. Patterson, and Eleanor B. Marr. Second Edition. John Wiley & Sons, Inc., New York, 1957. xv + 397 pages, $9.50.

Rectifying Semiconductor Contacts, by H. K. Henisch. Oxford University Press, New York, 1957. xii + 372 pages, $11.20.

Elements of Engineering Thermodynamics, by Rolf H. Sabersky. McGraw-Hill Book Co., Inc., New York, 1957. xvi + 318 pages, $7.50. A first course textbook.

* Order from Office of Technical Services, U.S. Dept. of Commerce, Washington 25, D. C.



Denver Post finds "Plus-4" Anodes do a better job of plating roto cylinders

The *Denver Post* is one of the few newspapers with its own rotogravure plant. Here it prints its *Empire* magazine and its comic section—also magazine sections for the *Seattle Times* and *Portland Oregonian*. It is noted throughout the Rocky Mountain area and the Northwest for its high-quality color printing.

Two years ago, the *Denver Post* switched to "Plus-4" Anodes in electroplating the printing surfaces of the rotogravure cylinders. The first result noticed was a big reduction in sludge and loss of copper in the solution.

The cylinders come out of the plating tank so uniform that it takes very little time to polish them. The finishers report the copper is good for tooling.

The copper printing surface is superior as far as uniformity and density are concerned. The cylinders hold up for the entire run—400,000 copies in the *Empire* run—and retain full quality in the light tones.

SEE FOR YOURSELF. A trial will show you how Anaconda "Plus-4" (Phosphorized Copper) Anodes can save you time and money—give you better work. Send the coupon today.

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In Canada: Anaconda American Brass Ltd., New Toronto, Ont.

Give me details on how I can get a test quantity of "Plus-4" Anodes sufficient to supply one tank.

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COMPANY.....
ADDRESS.....
CITY.....ZONE.....STATE.....

Scientific German, by G. E. Condoyannis. John Wiley & Sons, Inc., New York, 1957. x + 164 pages, $2.50.

Standard Samples and Reference Standards issued by the National Bureau of Standards, National Bureau of Standards Circular 552 (second edition), 24 pages, 25 cents. (Order from the Superintendent of Documents, Government Printing Office, Washington 25, D. C.) The Circular is also available without charge to prospective purchasers of Standard Samples, upon request to the National Bureau of Standards.

This Circular contains an up-to-date descriptive listing of the various Standard Samples issued by the National Bureau of Standards and supersedes Circular 552 issued in August 1954.

Note: Foreign remittances must be in U.S. exchange and should include an additional one-fourth of the publication price to cover mailing costs.

Wirkungsweise Aufbau und Behandlung von Elektrischen Akkumulatoren, by A. Ausderau, Boudry/Neuchatel, Switzerland. Fourth edition. Privately produced by mimeograph process, bound in hard covers, vii + 141 pages; separate booklet with 80 photographs and figures, 1956-57. No price given.

Practical treatise on lead and other storage cells.

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Please address replies to box shown, c/o The Electrochemical Society, Inc., 1860 Broadway, New York 23, N. Y.

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Address all correspondence to the Editor, JOURNAL OF THE ELECTROCHEMICAL SOCIETY, 1860 BROADWAY, NEW YORK 23, N. Y.

FORM

Manuscripts submitted for publication should be in triplicate to expedite review. They should be typewritten, double-spaced, with 2½-4 cm (1-1½ in.) margins.

Title should be brief, followed by the author's name and his business or university connection.

Abstract of about 100 words should state the scope of the paper and give a brief summary of results.

ILLUSTRATIONS

Drawings will be reduced to column width, 8.3 cm (3¼ in.), after reduction should have lettering at least 0.15 cm (1/16 in.) high. Original drawings in India ink on tracing cloth or white paper are preferred. Curves may be drawn on coordinate paper only if the paper is ruled in blue. All lettering must be of lettering-guide quality. See sample drawing on reverse page.

Photographs must be glossy prints and mounted flat.

Captions for all figures must be included on a separate sheet. Captions and figure numbers should not appear in the body of the figure.

General—Figures should be used only when necessary. Omit drawings or photographs of familiar equipment. Figures from other publications are to be used only when the publication is not readily available, and should always be accompanied with written permission for reprinting.

REFERENCES

Literature and patent references should be listed at the end of the paper on a separate sheet, in the order in which they are cited. They should be given in the style adopted by *Chemical Abstracts*. For example:

R. Freas, *Trans. Electrochem. Soc.*, **40**, 109 (1921).

H. T. S. Britton, "Hydrogen Ions," Vol. **1**, p. 309, D. Van Nostrand Co., New York (1943).

H. F. Weiss (To Wood Conversion Co.), U. S. Pat. 1,695,445, Dec. 18, 1928.

UNITS OF MEASUREMENT

Metric units should be used throughout but, where desirable, English units may be given in parentheses.

Corrosion rates in the metric system should preferably be expressed as milligrams per square decimeter per day (mdd), and in the English system as inches penetration per year (ipy).

As regards algebraic signs of potentials, the standard electrode potential for $Zn \rightarrow Zn^{++} + 2e$ is negative; for $Cu \rightarrow Cu^{++} + 2e$, positive.

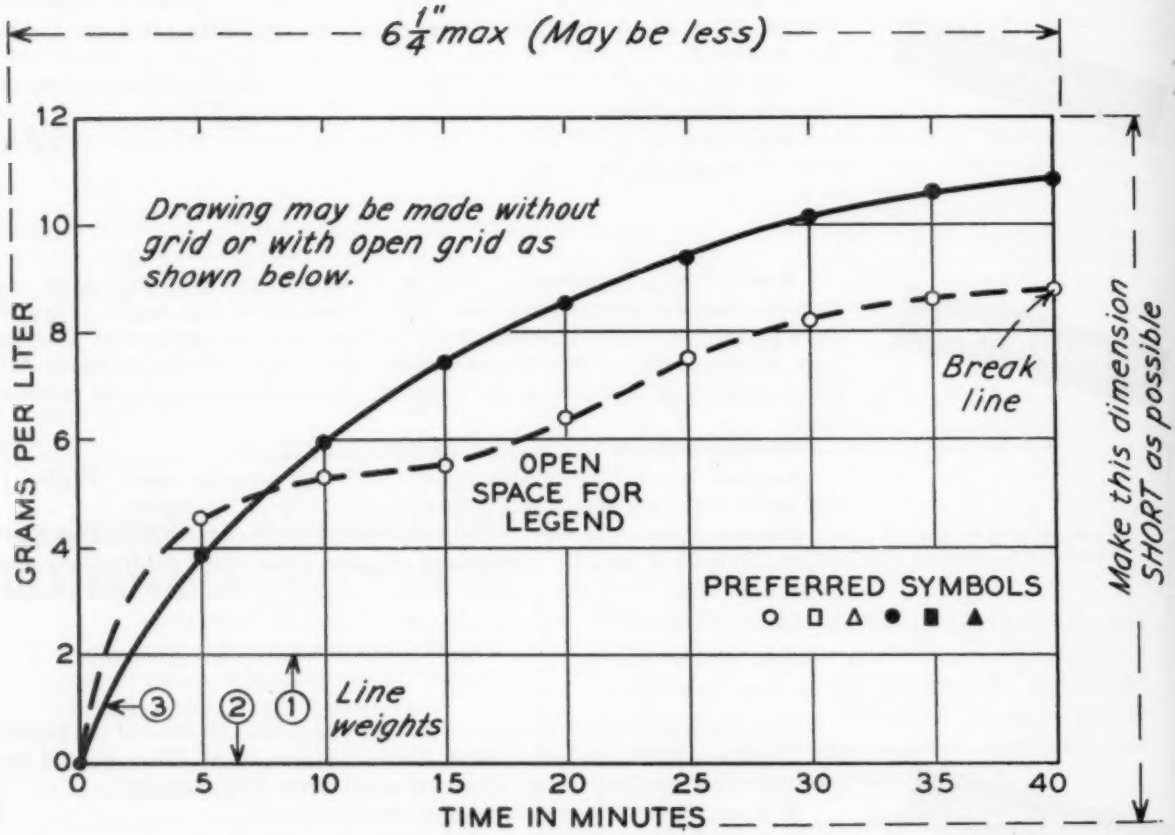
ABBREVIATIONS

Abbreviations should conform with the American Standards Association's list of "Abbreviations for Scientific and Engineering Terms."

GENERAL

Authors should be as brief as is consistent with clarity, and must omit all material which can be regarded as familiar to specialists in the particular field.

The use of proprietary names, trade-marks, and trade names should be avoided if possible. If used, these should be capitalized so that the owner's legal rights are not jeopardized.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